Combined forward osmosis-reverse osmosis for the treatment of brewery wastewater

Schneider, Carina; Zarebska, Agata; Hélix-Nielsen, Claus

Published in:
Proceeding for 11th International Congress on Membranes and Membrane Processes (ICOM 2017)

Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

[O6.22]

Organic solvent nanofiltration with novel perfluoropolymer and other polymeric membranes

J. Chau, P. Basak, K.K. Sirkar*
New Jersey Institute of Technology, USA

Introduction: For organic solvent nanofiltration (OSN), a variety of membranes have been investigated; their materials and structures include the following: poly(dimethylsiloxane) (PDMS); mixed matrix membranes of PDMS with zeolites/other fillers; asymmetric integrally skinned polyimide (PI) membrane crosslinked with aromatic/aliphatic diamines; polyaniline; polypyrrole; interfacially-polymerized polyamide with/without functionalized carbon nanotubes; carbon-based membranes. Most studies involved polymeric membranes. With demanding organic solvents aprotic/otherwise, most polymeric membranes have high/low swelling influencing their solute rejection behavior. Diamine-crosslinked PI membranes show excellent resistance to organic solvents but may swell in water. To this end we have started studying membranes from a particular class of fluoropolymers extremely inert to commonly-used solvents including aprotic ones; no crosslinking is needed.

Methods: Dense samples of an amorphous perfluoropolymer were studied for vacuum-driven pervaporation-based selective removal from organic-organic and aqueous-organic mixtures. OSN was implemented with composite flat membranes supported on an e-PTFE substrate with many solvents over a pressure range 1000-2500kPa. Composite membranes having two different perfluoropolymer coating-thicknesses, 0.6,1.6μm, were used. Solute rejection in methanol and THF were determined by two dyes, Brilliant blue R (826 Da) and Safranin O (351 Da). Solvent mixture compositions were characterized by GC.

Results: Permeation of many pure solvents were determined for OSN over a considerable pressure range. We report results of solvent flux and dye solute rejection for such membranes in composite form. Studies were made with solvent mixtures as well, e.g. n-heptane-toluene to investigate the application of solvent exchange. Solvent sorption studies were conducted as well with these polymers to develop a better understanding of the observed separation of the dye solutes and membrane transport. These membranes have excellent resistance to all solvents except perfluorosolvents. Other PI-based membranes were also studied for particular cases.

Discussion: This novel class of fluoropolymer membranes with extraordinary solvent resistance has good prospects for various applications in OSN.

Keywords: Organic solvent nanofiltration, Perfluoropolymer membrane, Organic dye solute rejection, Solvent mixture permeation

[O6.23]

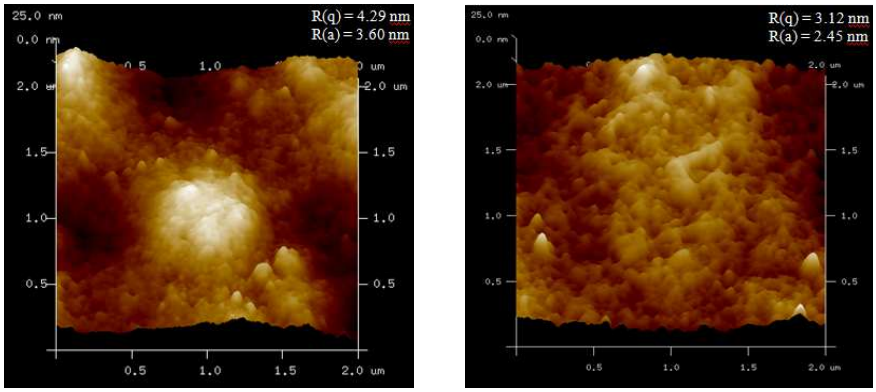
Developmentof Polyamide-imide Based Positively Charged Nanofiltration Membranes By a New Approach

A. Cihanoglu*, S.A. Altinkaya
Izmir Institute of Technology, Turkey

The aim of this research is to obtain polyamide-imide(PAI) based positively charged flat sheet nanofiltration(NF) membranes using a new approach which allows preparing the membranes in a single step. In this approach, positively charged polyelectrolyte polyethylene imine(PEI) was dissolved in the coagulation bath at ambient temperature and the casting solution containing no pore forming agent was immersed into the coagulation bath to achieve crosslinking between imide group in PAI and amine group of the PEI. The presence of PEI in the membranes and crosslinking were confirmed by FTIR,SEM,AFM and Zeta potential analysis.

In literature, generally, PAI based positively charged NF membranes are obtained by applying chemical post-treatment at high temperature which causes a damage of the pores on the bare membrane structure. Also the casting solution includes various pore forming agents such as EG,PEG and LiCl[1-2]. Due to uncontrolled leaching of these agents, it is not easy to acquire long term stable nanofiltration membranes. In our approach, there is no risk of changing the pore structure due to exposure to high temperature and chemical post-treatment is not needed. One of the other main advantages of this technique is that the surface tension of the coagulation bath decreases by dissolving PEI in the bath, providing the dense skin layer formation on the membrane surface due to the delayed demixing.

Four different neutral molecules (PEG1000,PEG600,sucrose and glucose) were used to determine pore size and MWCO of the membrane. Pure water permeability and molecular weight cut-off were found to be 3.88±0.044(L/m^{2}hbar) and 560 Da, respectively. AFM results in Fig.1 indicated that the roughness of the membranes decreased after crosslinking. The membranes can have potential e.g. for recovery of valuable cationic macromolecules.



a) b)

Fig.1 AFM images of PAI membranes (a) and PAI-PEI membranes (b) with scanned areas of 2 µm x 2 µm

Acknowledgements

One of the authors, Aydın Cihanoğlu, was supported by the Scientific and Technological Research Council of Turkey (TÜBİTAK) with (2211/E) National PhD Scholarship programme.

References

[1] S.P. Sun, T.A. Hatton, T.S. Chung, Hyperbranched polyethyleneimine induced cross-linking of polyamide-imide nanofiltration hollow fiber membranes for effective removal of ciprofloxacin, *Environ. Sci. Technol.,* 45 (2011) 4003-4009.

[2] Qiu, C., Setiawan, L., Wang, R., Tang, C.Y., Fane, A.G. High performance flat sheet forward osmosis membrane with an NF-like selective layer on a woven fabric embedded substrate, *Desalination,* 287 (2012) 266-270

Keywords: Positively charged nanofiltration, Poly(amide–imide), Flat sheet membrane, Polyethylene imine

[O6.24]

Effect of acidic dopants on the performance of polyaniline membranes in organic solvent nanofiltration

J. Shen*, S. Shahid, L. Xu, D.A. Patterson
University of Bath, UK

This study aimed to systematically understand the effect of acidic dopants on the performance of polyaniline (PANI) membranes in organic solvent nanofiltration (OSN). PANI has received ever-increasing attention in the field of membrane technology due to its intrinsic conductivity, synthesis simplicity, chemical and environmental stability. However, the applications of PANI membranes in OSN are still very limited.

PANI powder was synthesized by oxidative polymerization and integrally skinned asymmetric PANI membranes were fabricated using phase inversion by immersion precipitation. These were then doped with HCl, poly(4-styrenesulfonic acid) (PSSA) and poly(acrylamidomethylpropanesulphonic acid) (PAMPSA), respectively. FT-IR and XPS analysis confirmed the successful incorporation of acidic dopants in the PANI polymer matrix. SEM images showed that PSSA and PAMPSA made the skin layer of the PANI membranes tight and smooth without affecting the structure of the bulk support layer. Contact angle measurements revealed that the doped PANI membranes were more hydrophilic than the undoped PANI due to their hydrophilic acidic groups. Swelling tests showed that the doped PANI membranes had improved chemical stability in a wide variety of organic solvents, and their swelling degrees decreased as the MWs of the dopants increased.

The doped PANI membranes were tested in OSN experiments using isopropanol as the solvent and PPG as the MWCO probe molecule. The results demonstrated that acidic dopants played a key role in determining the porosity of the membranes. The PANI-PAMPSA membrane was found to have very high rejections in the NF range with an estimated MWCO of 360 g/mol. The PANI-HCl and PANI-PSSA membranes were found to have UF characteristics. This study has demonstrated that acidic doping is a key step to confer chemical stability and NF properties to the PANI membranes.

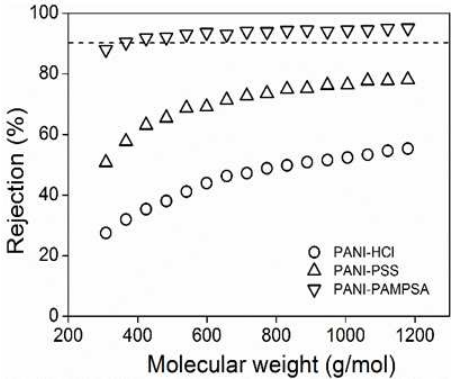


Figure 1: MWCO curves of PANI membranes with PPG/isopropanol solution at 30 bar and 25 °C

Keywords: polyaniline, organic solvent nanofiltration, dopant, molecular weight cut-off

[O6.25]

Composite membranes containing engineered porous materials for biogas purification

T.H. Bae*, Y. Yang, H. Gong, T.H. Nguyen

Nanyang Technological University, Singapore

Biogas produced in anaerobic digestion process has been considered as a renewable energy source. Although membrane technology is an ideal process for biogas recovery/purification, the applications have been limited by the unsatisfactory performance of commercial polymeric membranes under the biogas separation conditions such as low CO_2 partial pressure. Thus, improving the performance of current polymeric membranes, which are inexpensive and mechanically stable, may facilitate the application of membrane technology in large-scale biogas upgrading processes. To this end, we fabricated a series of mixed-matrix membranes by incorporating engineered porous materials that can selectively transport CO_2 into polymer matrices.

Recently, we have developed hierarchical mesoporous Ca-A zeolites with amine-appended mesoporous domain for application in post-combustion CO_2 capture. Owing to the contributions of both the active sites in Ca-A zeolites and the amine groups in mesoporous surfaces, the material exhibited an excellent CO_2 uptake property even at low CO_2 partial pressure. Moving forward, amine-appended hierarchical Ca-A was employed as a filler for mixed-matrix membranes to improve CO_2 selectivity. Gas permeation testing revealed that the amine-appended hierarchical Ca-A is highly efficient in enhancing CO_2/CH_4 selectivity of polymeric membranes.

We also explored the potential utility of porous layered material as a filler for composite membrane fabrication. In this work, 2-D metal-organic framework nanosheets with high-aspect-ratio were deliberately paired with polymers possessing high free volumes to fabricate high performance membranes. Owing to the molecular sieving effect the filler, a small filler loading (2-4 wt%) could significantly improve CO_2/CH_4 selectivities of membranes, resulting in the performance surpassed the upper bound limit for polymer membranes.

1. T. H. Nguyen, S. Kim, M. Yoon, T. H. Bae, *ChemSusChem,* **2016***, 9,* 455-461

2. T. H. Nguyen, H. Gong, S. S. Lee, T. H. Bae, *ChemPhysChem,* **2016***, 17,* 3165-3169

3. Y. Yang, K. Koh, R. Wang, T. H. Bae, *submitted*

Keywords: Biogas, Zeolite, Metal-organic framework, Layered material

[O6.26]

A new superior competitor for exceptional propylene/propane separations: ZIF-67 containing mixed matrix membranes

J. Lee*[1], H. An[1], H. Kwon[2], H. Jeong[2], K. Baek[3], S. Hong[3]

[1]Sogang University, Republic of Korea, [2]Texas A&M University, USA, [3]Korea Institute of Science & Technology, Republic of Korea

Recently, the ZIF-67 molecular sieve has emerged as an excellent substitute for the ZIF-8 counterpart due to its potentially high C_3H_6/C_3H_8 separation performance. Here, for the first time, we investigated the effect of ZIF-67 in mixed matrix membranes (MMMs) for C_3H_6/C_3H_8 separations by integrating them into 6FDA-DAM polymer matrix. The 6FDA-DAM/ZIF-67 (80/20 wt/wt) MMMs achieved an ideal selectivity of 29.9 and a separation factor of 19 under single and equimolar mixed gas conditions, respectively, at 35 °C. The intrinsic C_3H_6/C_3H_8 separation performance of ZIF-67 was estimated from our experimental transport results based on the Maxwell model. The calculation demonstrated its superior C_3H_6/C_3H_8 selectivity of 251, which is twice of that of ZIF-8, supporting the high molecular sieving capacity of ZIF-67 containing MMMs. Moreover, a thorough investigation on the temperature-dependent gas transports elucidated that the energetic selectivity is a major contributor for the high C_3H_6/C_3H_8 diffusivity selectivity in ZIF-67 containing MMMs. However, the minimum aperture size of ZIF-67 (4.5 Å), derived by the cuboid dimensions of C_3H_6 and C_3H_8, substantially sacrificed the C_3H_6/C_3H_8 entropic selectivity of ZIF-67 containing MMMs. Lastly, the defect-free incorporation of ZIF-67 nanoparticles into 6FDA-DAM polymer matrix effectively retarded physical aging process, maintaining the excellent separation performance of the associated MMMs for 75 days.

Keywords: ZIF-67, mixed matrix membranes, propylene/propane, physical aging resistance

[O6.27]

H_2/CO_2 Separation at elevated temperature with molecularly tuned free volume of vapor cross-linked 6FDA-Durene/ZIF-71 mixed matrix membranes (MMMs)

S. Japip*, K-S. Liao, T.S. Chung
National University of Singapore, Singapore

Membranes with attractive H_2/CO_2 separation properties at 150°C and thermally controlled free volume (FV) are the pre-requisites for their industrial application in pre-combustion CO_2-removal processes. We report, for the first time, the H_2/CO_2 separation properties of di/tri-amine vapor cross-linked mixed matrix membranes (MMMs) with tunable FV at elevated temperatures up to 150 °C. FV of cross-linked MMMs was molecularly tuned by altering the degree of chain motion using ethylenediamine (EDA), diethylenetriamine and tris(2-aminoethyl)amine.

While both thermal gravimetric analyzer coupled with Fourier-transform infrared spectrometer (TGA-FTIR) and X-ray photoelectron spectrometer (XPS) confirm the relatively high thermal stability of the TAEA vapor cross-linked MMM without experiencing the reversed diamine cross-linking reaction at 150 °C, both EDA and DETA vapor cross-linked MMMs reveal contrasting behavior. Nevertheless, the EDA vapor cross-linked MMM demonstrates the highest H_2/CO_2 selectivity owing to the smallest shift of free volume distribution when the operating temperature was increased from 35 to 150 °C. Both CO_2 adsorption isotherms and positron annihilation lifetime spectroscopy (PALS) conducted at 35 °C and 150 °C elucidated the degree of chain motion and the molecularly tuned FV in the cross-linked MMMs. A more restricted degree of chain motion was achieved in the cross-linked network and the resultant membrane has a lower H_2 permeability but a higher H_2/CO_2 selectivity at 150 °C.

Among the vapor cross-linked MMMs, the EDA-treated MMMs was distinguished for the best H_2/CO_2 separation performance with an H_2 permeability of 141 Barrer and an H_2/CO_2 selectivity of 11.6 at 150 °C. Furthermore, the presence of ZIF-71 inside the EDA vapor cross-linked MMM provides additional sites for generating EDA vapor cross-linked network. Therefore, the observed molecularly-tuned free volume of vapor cross-linked 6FDA-Durene/ZIF71 MMMs may originate from the coupling of both the cross-linkers chain motion and the additional network surrounding ZIF-71.

Keywords: high temperature hydrogen separation, cross-linker chain motion, tunable free volume, vapor cross-linking

[P2.067]

Flexible semi-ceramic semi-rubbery M_xO_y-PDMS composites with high gas permeability

R. Selyanchyn*, S. Fujikawa

Kyushu University, Japan

CO_2 gas capture with the usage of membranes is a challenging task but also a promising approach for industry as it has potential to reduce capture costs to the economically feasible values. Performance of organic polymers is limited by trade-off relation between permeability and selectivity as well as negative effects such as physical aging or plasticization. In order to utilize highly selective state-of-art materials, ultimate thinning of membranes is required to provide fluxes suitable for industrial applications which in turn leads to higher probability of microdefects and accelerated physical aging. Therefore, new materials with suitable permeability and selectivity for target gases are still required.

In our work we have studied the potential of amorphous metal oxide membranes for CO_2/N_2 gas separation. For instance, we investigate the formation of the metal oxide (TiO_2, ZrO_2) cross-linked PDMS using the in-situ sol-gel of alkoxides with silanol terminated PDMS. Figure 1a shows the structural concept of fabricated hybrid materials sometimes referred as flexible ceramics. Physical properties of hybrids were strongly influenced by two factors – content of the metal oxide and molecular weight of precursor PDMS-OH (Fig. 1b). Notably, prepared membranes demonstrated superior gas separation performance compared to conventional PDMS i.e. both selectivity and permeability improved (e.g. Fig.1c for CO_2/N_2 pair separation using TiO_2@PDMS and ZrO_2@PDMS membranes). Due to high gas permeability, developed materials can be used independently or as gutter/caulking layer in composite membranes – alternatively to conventional polymers.

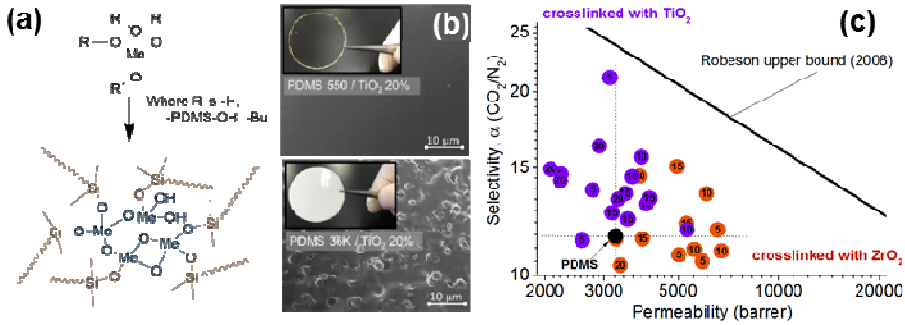


Figure 1. (a) Principle of metal oxide-PDMS composite (flexible ceramic) material formation; **(b)** morphology of membranes with different M_w of PDMS-OH cross-linked with 20 wt% TiO_2; **(c)** CO_2/N_2 separation performance of TiO_2 (blue circles) and ZrO_2 (red circles) cross-linked PDMS-OH compared to conventional PDMS.

Keywords: high gas permeability, CO2 capture, flexible ceramics, hybrid materials

[O5.18]

Can graphene-based nanofillers reduce the ageing of high free volume glassy polymers?

L. Olivieri[1,2], S. Meneguzzo[1], M.G. De Angelis*[1,2], S. Ligi[3], A. Saccani[1], L. Giorgini[1]
[1]University of Bologna, Italy, [2]INSTM, Italy, [3]GNext SAS, Italy

Few-layer graphene and graphene oxide nanoplatelets were incorporated in a solution of a high free volume glassy polymer (PTMSP), that is prone to ageing. The solutions were used to form thick membranes (60-180 □m) via solvent casting, (Fig. 1a), [1] as well as thinner films (1-10□m) spin-coated onto microporous supports. (Fig. 1b)

The permeability of He, N_2, CH_4 and CO_2 was measured at 35°C, as a function of time. The addition of graphene moderately lowers the permeability to all gases, while graphene oxide slightly enhances it. A reproducibility analysis was performed and it was found that, although the quantitative variations of permeability vary from sample to sample, the qualitative behavior is similar for a same type of filler.

Ageing kinetics of PTMSP is known to be a strong decreasing function of thickness[2]: therefore, the permeability decay was reported versus the quantity [time/thickness^2]. The addition of nanofillers lowers the slope of gas permeability decay by factors as high as 2, i.e. it allows to reduce the ageing drift of PTMSP. Graphene is slightly more effective than graphene oxide in reducing ageing. The ageing kinetics of PTMSP is gas-dependent, and the extent of ageing reduction provided by the filler also depends on the gas type. In particular, the 'stabilization effect' is higher for CO_2 permeability, followed by CH_4, N_2 and He. Such trend, shown in Fig. 1c) has a beneficial effect on the long-time CO_2/CH_4, CO_2/N_2, CO_2/He selectivity. The effects observed with graphene are higher than those observed with metal oxide particles,[3] indicating that graphene efficiently inhibits the polymer rearrangement that causes ageing , in both thick and thin films.

1. L. Olivieri et al., *Ind. Eng Chem Res* 54 (2015) 11199 - 11211.

2. K.D. Dorkenoo et al. *Macromolecules* 33 (2000) 3747-3751.

3. S. Matteucci et al., *Polymer* 49 (2008) 1659-1675.

Fig 1a) Thick Mixed Matrix Membranes (60-180 microns)

Preparation protocol PTMSP+graphene

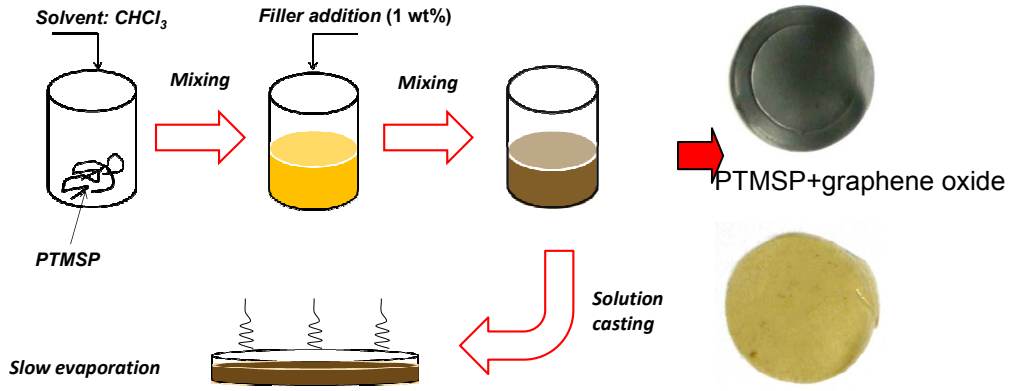


Fig 1b) Thin Mixed Matrix Membranes (1-10 microns) over a Porous support

Preparation protocol: SEM cross section

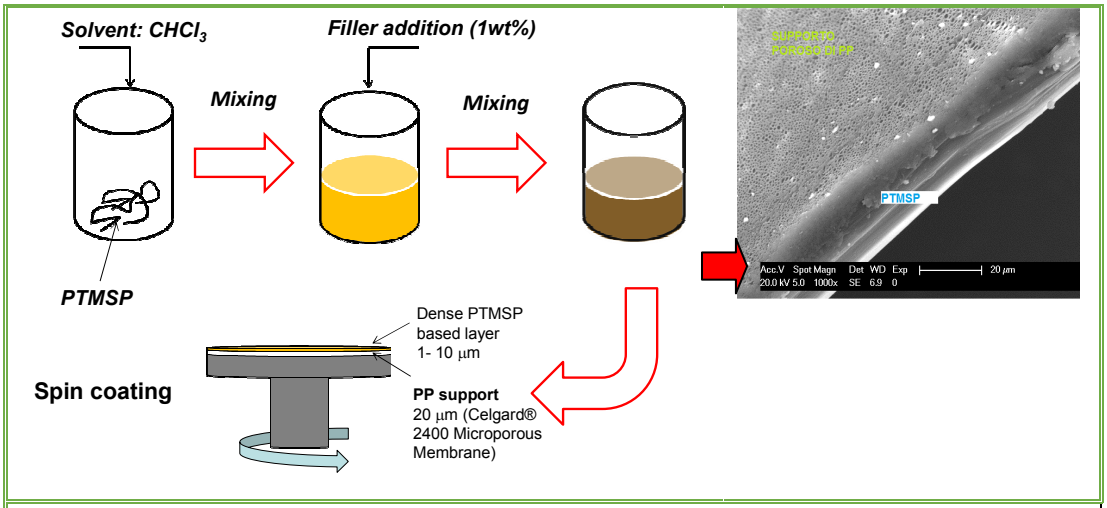


Fig 1c) *n*=ageing index=slope of permeability decay versus (time/thickness^2)

n	He	N_2	CH_4	CO_2
PTMSP	0.33	0.37	0.45	0.47
PTMSP+GO	0.23	0.34	0.40	0.21
PTMSP+GRES	0.20	0.28	0.28	0.19

Keywords: graphene, glassy polymers, ageing, gas separation

[O6.30]

Gas separation performances of 6FDA-based polyimide mixed matrix membranes with high surface area UiO-66 (Zr-BDC) nanoparticles

M.Z. Ahmad*[1,2], M. Navarro[2], B. Zornoza[2], J. Coronas[2], C. Tellez[2], V. Fila[1]

[1]*University of Chemistry and Technology Prague, Czech Republic,* [2]*University of Zaragoza, Spain*

Metal-organic frameworks (MOFs) incorporation into mixed matrix membranes is gaining more attention due to its combined advantages of high separation performance and easy processability. High surface area CO_2-philic zirconium MOF, UiO-66 (Zr-BDC), was synthesized with BET surface area of 902 $m^2.g^{-1}$ and incorporated into three 6FDA-based co-polyimides (namely 6FDA-BisP, 6FDA-ODA, and 6FDA-DAM) with the loadings between 5 – 20 wt. %. The nanoparticles and MMMs were characterized accordingly by XRD, SEM (Fig. 1a), TEM, FTIR, and TGA. CO_2 and CH_4 isotherms on the nanoparticle were measured by a static volumetric method at the pressure up to 10 bar. Fractional free volume (FFV) was calculated using solid density property, measured by pycnometer. Gas separation performance was evaluated using feed composition of 50%:50% CO_2:CH_4 binary mixture at 35°C and a pressure difference of 2 bar. Both CO_2 permeability and selectivity of 6FDA-BisP (pristine performances of $\alpha_{CO2/CH4}$ = 27.5 ± 4.4, ρ_{CO2} = 33.9 ± 2.9 Barrer) were improved by 52% and 217%, respectively with 15 wt. % loading (See Fig. 1b). Meanwhile, we observed an increment of 180% and 68% for CO_2 permeability and selectivity for 6FDA-ODA (pristine performances of $\alpha_{CO2/CH4}$ = 20.6 ± 2.0, ρ_{CO2} = 25.9 ± 3.0 Barrer) at the same loading. CO_2 permeability also increased by 92% for 6FDA-DAM (pristine performances of $\alpha_{CO2/CH4}$ = 29.2 ± 3.1, ρ_{CO2} = 997.0 ± 49.7 Barrer) with 20% UiO-66 loading, while maintaining the CO_2/CH_4 selectivity. The incorporation of UiO-66 into these co-polyimides has significantly improved gas separation performances, offering a promising potential for future CO_2 capture membrane based technologies.

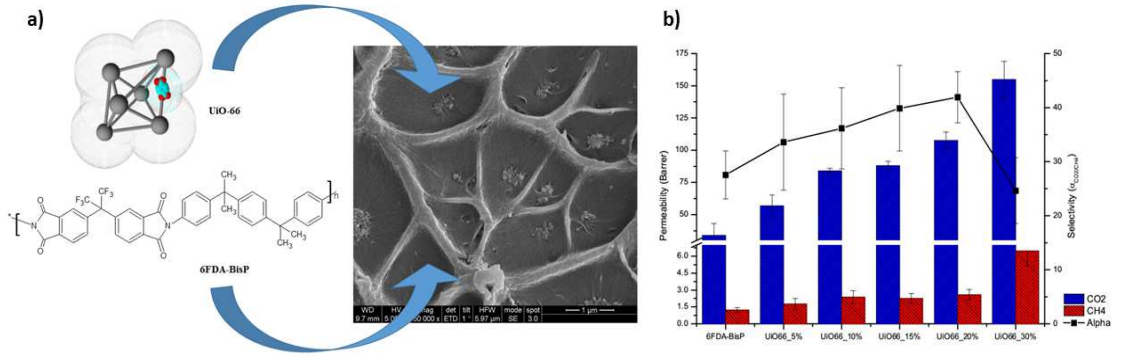


Figure 1: The incorporation of UiO-66 into 6FDA-based co-polyimide mixed matrix membranes. (a) SEM image of 6FDA-BisP-UiO66-5%, and (b) 6FDA-BisP-UiO66 MMMs gas separation performance.

Keywords: CO2 separation, 6FDA-based copolyimide, metal organic framework, UiO-66

[O5.37]

Effect of gas phase impurities on carbon dioxide separation in mixed matrix membranes

S. Kanehashi*[1,2], A. Aguiar[2], H. Lu[2], S. Kentish[2]

[1]Tokyo University of Agriculture and Technology, Japan, [2]The University of Melbourne, Australia

Mixed Matrix Membranes (MMMs) combine the benefits of both polymer substrates and inorganic/organic fillers and have become attractive materials for gas separation in recent years [1-3]. In this work, a series of mixed matrix membranes were prepared using the aromatic polyimide Matrimid and porous nanoparticles including a porous carbon, a porous organic polymer (POP) and two metal organic frameworks (MOFs). We show that common impurities found in power station flue gases (H_2S, SO_2, and NO) have significant effects upon the performance of these mixed matrix membranes. The effects of NO, SO_2 and H_2S on ZIF-8 are all large and rapid and would render these membranes unsuitable for flue gas service. Similarly, H_2S appears to adsorb irreversibly into membranes containing Cu-BTC, although the impacts of NO and SO_2 are less severe. The membranes containing POP-2 or porous carbon are less affected by these contaminants. This probably reflects the fact that these additives do not contain a reactive metal atom within their structure. In particular, the permeability of the membrane containing POP-2 is still significantly above that of the base Matrimid polymer after exposure for 80 days to 1000 ppm of each contaminant. These results suggest that MMMs prepared using organic nanoparticles such as carbon and POP can be effective in gas separation applications such as natural gas sweetening, biogas purification and post-combustion carbon capture, when these impurities are present.

References

1. **S. Kanehashi**, G. Chen, C. Scholes, B. Ozcelik, C. Hua, L. Ciddor, P. Southon, D. Alessandro, S. Kentish, Enhancing gas permeability in mixed matrix membranes through tuning the nanoparticle properties, *J. Membr. Sci*., **482**, 49-55 (2015).

2. **S. Kanehashi**, G. Chen, L. Ciddor, A. Chaffee, S. Kentish, The impact of water vapor on CO_2 separation performance of mixed matrix membranes, *J. Membr. Sci*., **492**, 471-477 (2015).

3. C. Lau, K. Konstas, C. Doherty, **S. Kanehashi**, B. Ozcelik, S. Kentish, A. Hill, M. Hill, Tailoring physical aging in super glassy polymers with functionalized porous aromatic frameworks for CO_2 capture, *Chem. Mater*., **27**, 4756-4762 (2015).

Keywords: Mixed matrix membrane (MMM), SO2, H2S, Metal organic framework (MOF)

[O6.32]

Understanding polymer confinement effects in ZIF-11 MMMs

E.Z. Zhou*, R.P.L. Lively

Georgia Institute of Technology, USA

Mixed matrix membranes containing zeolitic imidazolate frameworks are an attractive alternative to conventional thermal separation processes. However, the interaction between the ZIF fillers and polymer matrix remains unclear. This work aims to develop ZIF-11-loaded mixed matrix membranes with enhanced separation performance by utilizing the fundamental understanding of the interplay between two phases. We believe that the separation performance of such membranes is highly interplay-dependent, and that proper selection of materials and rational modification of the fabrication procedure will enhance membrane performance.

To better understand the interplay between two phases, volumetric dosing adsorption, pulsed field gradient-nuclear magnetic resonance, and isochoric permeation system are utilized for the characterization of these materials. To develop quantitative structure property relationships, solid-state NMR techniques are applied to explore and quantify the influence of polymer confinement of ZIF-11 crystals. With the understanding of the interplay between ZIF-11 fillers and polymer matrix, mixed matrix membrane is fabricated with optimized separation performance.

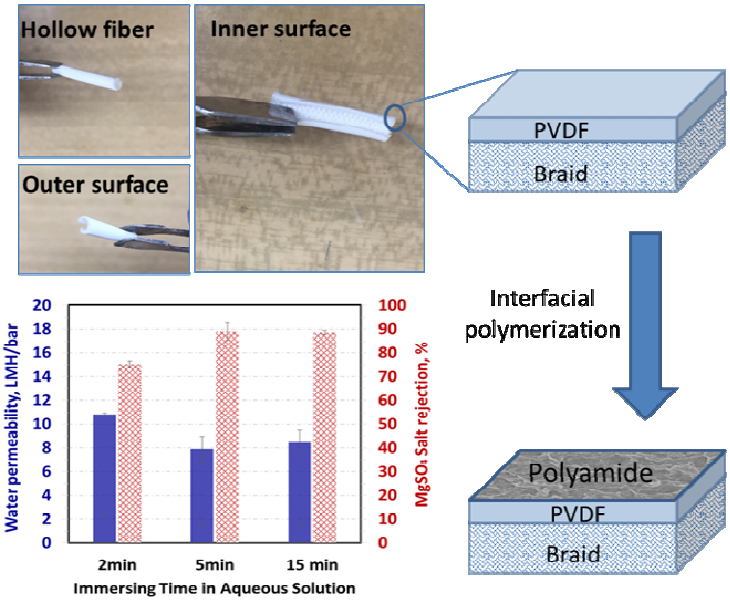
Keywords: ZIF, Confinement, NMR

[O6.33]

Braided-reinforced thin film composite (TFC) nanofiltration hollow fiber membranes

J.R. McCutcheon, L. Xia*
University of Connecticut, USA

Hollow fiber membranes are attractive for use in water treatment processes because of their high packing density relative to flat sheet and spiral wound configurations. They are also easily submersed in tanks for bioreactor applications. For water purification in particular, they are commonly use in microfiltration (MF) an ultrafiltration (UF) applications. To enable low pressure drop in fiber lumens, inner diameters of these fibers can be rather large, thus limiting the pressure tolerance of these membranes. Low pressure tolerance of larger capillary fibers has largely excluded the use of hollow fiber from higher pressure membrane processes reverse osmosis (RO) and nanofiltration (NF) except for cases where integrated asymmetric membranes are considered. Use of the thin-film composite (TFC) platform with polyamide based selective layers, while common with flat sheet membranes for RO an NF, have not found commercial success and have largely been relegated to the academic community for studies on forward osmosis (FO). In this work, we show that hollow fiber TFC membranes can be made for higher pressure applications. To address the pressure tolerance issues, we build our TFC using a commercial hollow fiber PVDF UF membrane that is reinforced with an embedded braid as a support. Onto this support is formed the selective barrier layer *in-situ* that from piperazine (PIP) an trimesoyl chloride (TMC) monomers. Through careful optimization the monomer concentration and reaction conditions, we have demonstrated softening with a 89 % $MgSO_4$ rejection and a permeance of 8 LMH/bar. This work represents the first time such a reinforce hollow fiber membrane has been used as a support for a TFC membrane and could broaden opportunities for hollow fiber membranes in processes where salt selection (RO, pressure retarded osmosis) is required.



Keywords: Hollow fiber membrane, Nanofiltration

[O6.34]

Amphiphilic PVC-based nanofiltration membrane: From molecular designing to membrane manufacture

M.Y. Zhou*[1], L.F. Fang[1,2], C.C. Sun[1], B.K. Zhu[1]
[1]Zhejiang University, China, [2]Kobe University, Japan

The PVC-based nanofiltration membrane with positive, negative or absent charges was fabricated from PVC-based amphiphilic copolymers (seen in the Figure 1) by surface coating, direct immersion annealing (DIA), crosslinking reaction or post-crosslinking after blending with other coploymer (Blend-CL). The amphiphilic copolymers with different charged group and different pH tolerance were synthesized by emulsion polymerization or atom transfer radical polymerization (ATRP). Thin film composite nanofiltration membranes were stacked through a single or several layers nanoparticle under 10 nm when coating the PVC-based emulsion particle such as P (VC-DMC), P (VC-AMPS), P (VC-SBMA) and P (VC-EG). However, with the weak pH tolerance, the molecule chains can be collapsed to fabricate a stable, defect-free, smooth and more dense film on the top surface nanofiltration separation layers when dipped in suitable non-solvent (DIA method) above their glass transition temperature (T_g) only 1 minute, in which the pore size of the membrane was tailored from about 10 nm to about 1 nm. Moreover, post-crosslinking on the surface of ultrafiltration membrane is also a universal method to fabricate nanofiltration. The PVC-based copolymer or PVC blending with other amphiphilic copolymers can also form the different charged nanofiltration membrane with the surface post-crosslinking. With different surface chemical compositions and structures, these membranes with nano-meters level pore can express the positive or negative nanofiltration property with the high separation ratio for the positive and negative ions due to Donnan repulsion and aperture sieving. Overall, this provides the flexibility to fabricate nanofiltration membrane using PVC-based amphiphilic copolymer without complicated process such as interfacial polymerization, which also enables production of advanced membranes with wide tunability, fast, low cost, and varying performance.

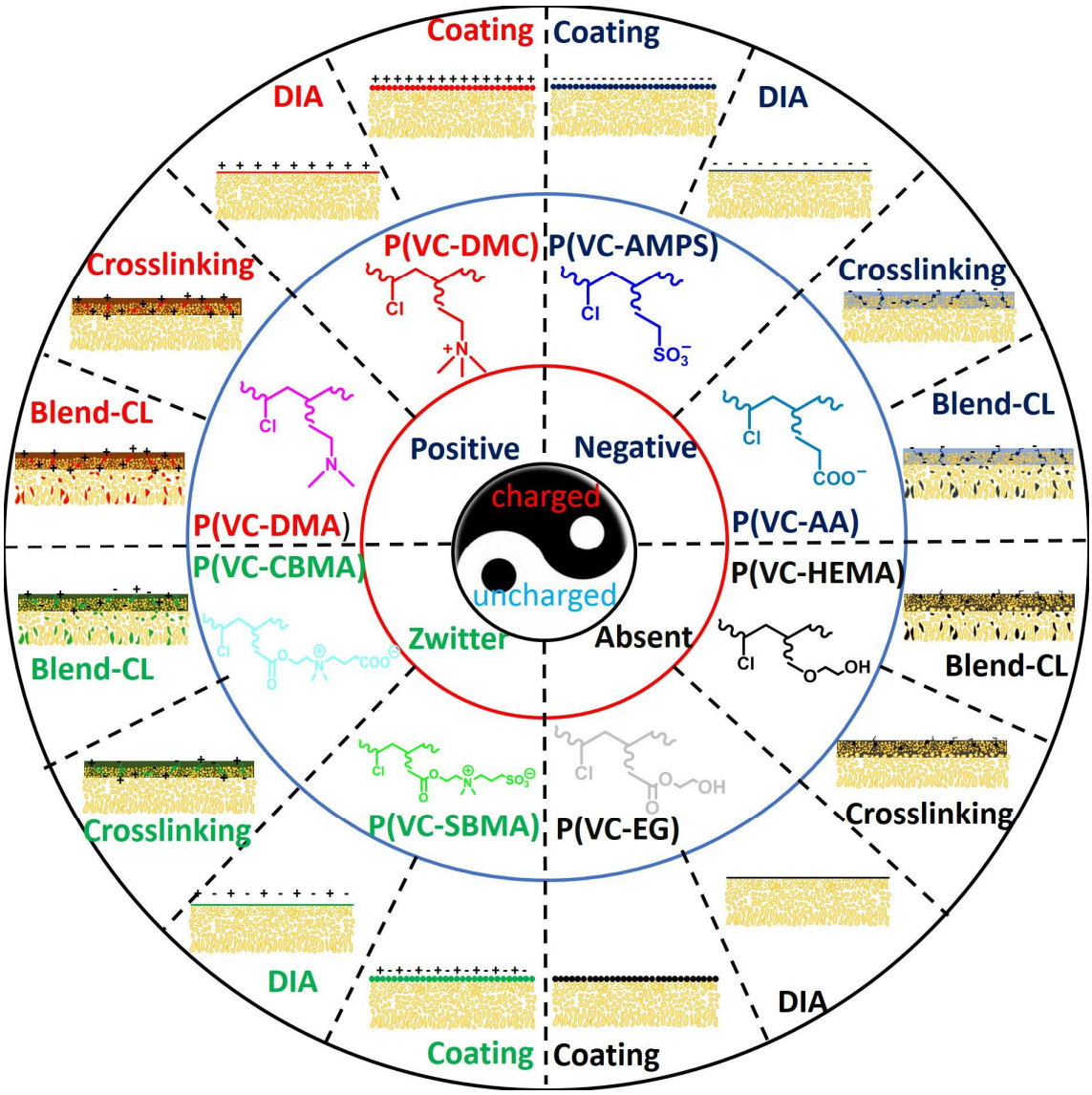


Figure 1. PVC-based nanofiltration membrane: from molecular designing to membrane manufacture

Keywords: Amphiphilic copolymer, molecular designing, membrane manufacture, nanofiltration

[O6.35]

Polyelectrolyte based hollow fibre membrane for various low-pressure nanofiltration applications

C. Liu*, T.H. Chong, R. Wang
Nanyang Technological University, Singapore

1. Introduction

Recently, a novel type of polyelectrolyte based hollow fiber nanofiltration (NF) membrane has been developed at the Singapore Membrane Technology Centre (SMTC). The layer-by-layer (LBL) polyelectrolyte deposition and chemical crosslinking was adopted to form an ultra thin selective layer on a porous polyethersulfone substrate. Promising results have been observed in various low-pressure (<5 bar) NF applications.

2. Methods

The membrane modification process will be briefly described and followed by the presentation of experimental results of three major applications. (i) In the seawater pre-treatment study, the membrane was tested at elevated concentrations of synthetic sea water to simulate the scenarios where large scale NF modules were operated at different recovery levels. (ii) The NF membranes were also incorporated in a bioreactor i.e. NF-MBR for municipal wastewater treatment to improve the quality of MBR permeate for further water reclamation process. (iii) Finally, 2-inch membrane modules were used to pre-treat over 100 litres of impaired water for further usage as the feed solution in the pressure retarded osmosis (PRO) process.

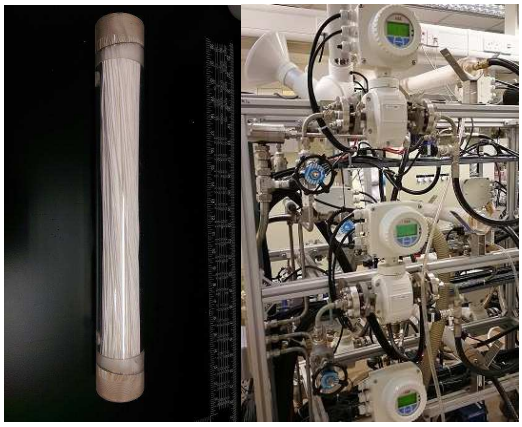


Figure 1. 2 inch membrane modules operated on a pilot test rig

3. Results and Discussion

(i) Approximately 60% recovery level was simulated for two types of NF hollow fibers. Both membranes have modest flux and superior hardness removal compared to commercial NF membranes as shown in Table 1.

Table 1 Summarized synthetic seawater test results for NF hollow fibres and commercial NF membranes (operating pressure = 4 bar)

	Recovery rate (%)	Average water flux* (LMH)	Overall Mg rejection* (%)	Overall Ca rejection* (%)
LBL A	65.7	8.2	88	66.2
LBL B	55.8	6.7	93.5	80.4
Commercial A	Around 50	12.3	69.2	44.2
Commercial B	Around 50	13.5	49.5	35.9
Commercial C	Around 50	5.2	77	57

(ii) In the NF-MBR system, 99 % removal of organic compounds was achieved. The improved MBR permeate was found to be beneficial in reducing the fouling of subsequent RO membrane in the water reclamation process as shown in Figure 2.

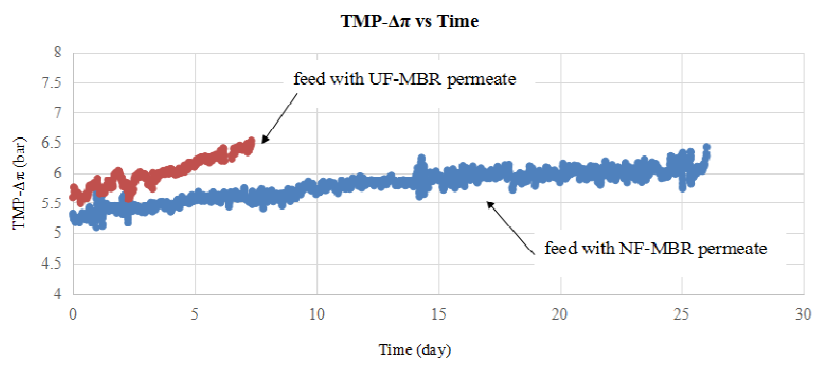


Figure 2. TMP profile of the RO system fed with permeates from NF-MBR and UF-MBR over 25 days

(iii) Considerable amount of organic and inorganic foulants were removed in the impaired water (Table 3). Thus the PRO flux could reach 30.5 LMH at 16 bars, which showed a significant improvement compared to only 9 LMH at 16 bars when using un-treated water.

Table 2 Water quality of PRO feed solutions

Samples	Ion removal (%)				Carbon content removal (%)		Conductivity reduction (%)
	Ca	Mg	SO4	PO4	TC	TOC	
Commercial NF P	49.8	48.0	95.6	74.8	37.0	70.3	11.1
2-inch module P	96.5	100	97.1	72.7	69.4	90.9	43.2

4. Conclusions

The newly developed polyelectrolyte based hollow fiber nanofiltration membranes have shown superior performance in various low-pressure NF applications.The capability to fabricate 2-inch membrane modules also proved their scalability and great potential for real applications.

Keywords: low-pressure nanofiltration, polyelectrolyte membrane, wastewater treatment, seawater pre-treatment

[O6.36]

Diananofiltration, a purification approach towards the sustainability? A green chemistry case study

A.R.S. Teixeira*[1,2], G. Willig[1,2], J. Couvreur[1,2], A.L. Flourat[1,2], A.A.M. Peru[1,2], P. Ferchaud[3], H. Ducatel[3], F. Allais[1,2]

[1]AgroParisTech, France, [2]Université Paris-Saclay, France, [3]Extractis, France

Select a purification method is not always trivial and straightforward. Technical feasibility of scaling-up and overall yield must be assessed. In the end, all decisions should be justified, including environmental sustainability. Here is presented a green chemistry case study.

Our laboratory developed a new class of non-toxic and renewable bisphenols able to substitute bisphenol A, exhibiting potent antioxidant activity, produced from ferulic acid through enzymatic pathways. Flash chromatography on silica gel is an efficient laboratory technique widely used, however, it is technically unfeasible at kilolab scale. On the other hand, recrystallization is one of the oldest and common purification processes. However, this technique is known for generating large volumes of mother liquors, usually discarded as waste, and depending on the target molecule solubility, yield losses can be significant. Solvent resistant nanofiltration (SRNF) is a straightforward technology for separate solutes present in an organic solvent as well as for solvent recovery. This work, compares all those purification approaches to produce *bis-O-dihydroferuloyl-1,4-butanediol* (BDF), one of these promising renewable bisphenols.

To assess SRNF, 6 commercial membranes were evaluated. Starting from an acetone-based solution (1g/L) containing 80:20 of BDF and EtDFe (ethyl dihydroferulate), a reagent in excess, GMT-oNF1 showed to be able to discriminate them. A two-stage diafiltration (TSD) in cascade was proposed, being observed an increase in the product yield (from 77% in a single stage to 95%). Since solvent recycling has a significant impact on sustainability, an additional nanofiltration step was assessed. 90% of the solvent was recovered with 1% of impurities. Recrystallization and filtration were compared by green metrics and LCA. Results showed that only the integration of solvent recycling in TSD process and the use of a concentrated starting solution (150g/L instead 1g/L) may lead to similar magnitude values observed for recrystallization, even being a less energetic intensive (4-fold).

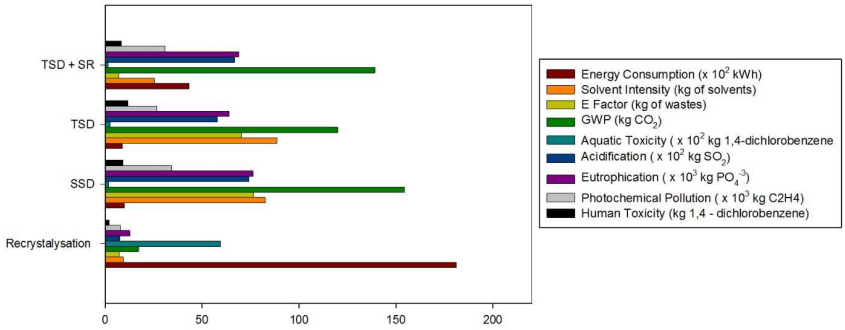


Fig. 1 Comparative environmental impact between the different processes: Recrystallization, SSD, TSD and TSD + Solvent Recovery (SR)

Keywords: Solvent Resistant Nanofiltration, Green Chemistry, Environnemental Sustainability, Solvent Recycling

[O6.37]

Graphene oxide membranes on inner surface of ceramic tubes for efficient water purification

M. Zhang*, J. Shen, G. Liu, J. Zhao, W. Jin

Nanjing Tech University, China

Graphene oxide (GO) is an emerging 2D building block for membranes featuring distinct laminar structure and tunable physicochemical properties. GO nanosheets can be stacked into well-ordered laminar structures, providing fast and selective 2D water-transport nanochannels, which makes GO membrane a very promising candidate for water purification. However, most of GO-based membranes are free-standing or polymeric supported, which limits their practical application. Compared with polymeric supports, the strength and availability of GO-based membranes can be improved by ceramic supports. Preparing membranes on inner surface of supports is more attractive because it can prevent the separation layer against handling damage. This achievement also provides a scalable strategy for the GO-based membranes since the ceramic tube can be easily replaced by state-of-art multi-channels ceramic products. We present here a scalable fabrication of GO membranes on inner surface of ceramic tubes for efficient water purification. Nanochannels within GO membranes including in-plane slit-like pores and plane-to-plane interlayer-galleries can be finely tailored by controlling lateral size and surface oxygenated functionalities of GO nanosheets. The substrate effect on GO membranes is also systematically optimized so as to realize high separation performance with good operation stability. The as-fabricated GO membranes exhibited high water permeability (3.4-27.1 L m^{-2} h^{-1} bar^{-1}) and excellent rejections for various organic matters and ions (>99% of organic dyes, >85% of Na_2SO_4, >98% of heavy metal ions), owing to the synergistic effect of molecular sieving and electrostatic interaction. Overall, our work provides an industrially preferred fabrication of GO membranes on inner surface of ceramic tubes for efficient water purification, which is believed as a notable step toward the practical application of GO-based membranes.

Keywords: Graphene oxide, Membrane, Ceramic support, Water purification

[O6.38]

Modelling concentrated multicomponent mixtures of non-spherical molecules for nanofiltration applications

V. Aguirre Montesdeoca*[1,2], A. Van der Padt[1], R.M. Boom[1], A.E.M. Janssen[1]
[1]Wageningen University, The Netherlands, [2]Institute for Sustainable Process Technology, The Netherlands

Nanofiltration applications are not restricted to water treatment, its potential is also used in food and biotechnology processes for the purification and concentration of streams. To represent these processes, available models are derived regularly based on simplified considerations such as solutes spherical shape, single solute mixtures and diluted conditions. Many industrial applications, however, do not comply with these simplifications making the design and control of these processes difficult. Therefore, a more rigorous and mechanistic transport model for the representation of industrial nanofiltration applications is needed.

The objective of this study was to adapt existing mass transport equations to more realistic considerations, namely: non-spherical molecules, multicomponent mixtures and concentrated conditions. The model was then validated with experiments using a mixture of fructo-oligosaccharides with a degree polymerization in a range of 1 to 8, where the intention was to remove the mono and di-saccharides from this mixture.

All three considerations described above were found to have significant effects on the system. Molecules with a degree of polymerization of 2 or higher where considered as capsules. This consideration had a great impact on the calculation of the hydrodynamic coefficients inside the membrane, leading to a higher rejection compared to spheres with the same volume. Furthermore, due to the high concentration of accumulated solutes near the membrane, a volume exclusion effect took place right outside the membrane. As a result, negative rejection values were obtained for the smaller molecules. This has to be taken into account for an efficient purification process, opening new possibilities for future improvements.

Keywords: Multicomponent solutions, Highly Concentrated solutions, Non-spherical molecules, Oligosaccharides purification

[O6.39]

Nanofiltration of dicarboxylic acids: How does pH affect permeabilities and rejections?

P.A.B. Díaz, A.C. Habert, F.A. Kronemberger*
Federal University of Rio de Janeiro, Brazil

Fermentation is an alternative for the large-scale production of dicarboxylic acids. But the production itself and the downstream processing of the fermentation media still need improvement. Nanofiltration has been studied as a post-fermentation step to recover unconverted carbon sources, enhancing acid productivity. In this work, the effect of a few process variables was evaluated in the nanofiltration of succinic acid solutions. Rejection and permeate fluxes were analyzed, together with membrane characterization results and acid dissociation profile. The acid rejection and permeation flux data are well described by the Kedem-Katchalsky model. It was observed that pH presented a major effect in the acid rejection, since both acid and membrane are subjected to its influence. Considering low pH values, where the acid is non-dissociated and uncharged, its rejection is related primarily to size exclusion and only 10-20% of the solute was retained. But rejections higher than 90% were obtained when pH was increased to 7.6, at which the acid is completely dissociated, clearly indicating a major effect of electrostatic repulsion. This result is presented in Figure 1 for the NFX membrane (Synder® Filtration).

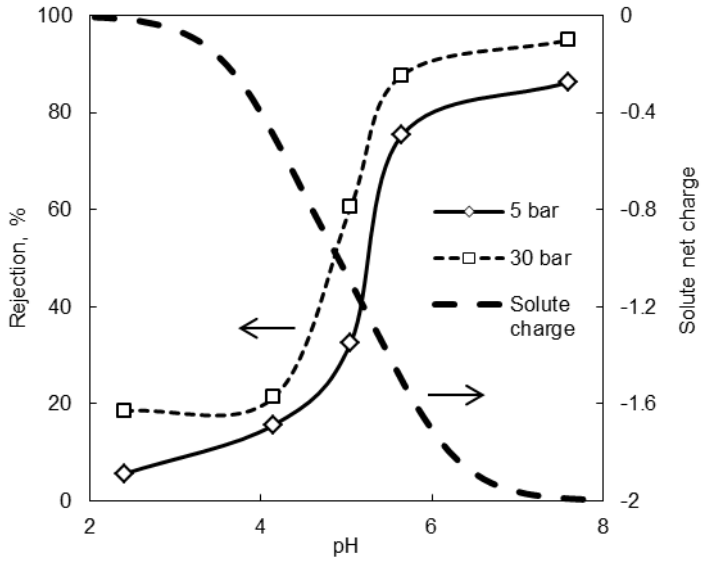


Figure 1: Succinic acid rejection and solute net charge variation with feed solution pH.

Furthermore, interesting results were observed when permeate fluxes were evaluated. Taking into account the effective pressure difference, deducting the osmotic pressure values, it seems that a slight membrane modification is occurring when increasing pH, enough to increase membrane permeability. All results can be discussed in terms of size and electrostatic exclusion mechanisms that take into account solute-membrane interactions and their variation according to the feed solution pH value. The results indicate that nanofiltration can indeed be applied in the recovery of unconverted carbon sources that are retained by the membrane, but only at low pH values, ensuring that the acid permeates loosely.

Keywords: Nanofiltration, Organic acid, Electrostatic repulsion, pH variation

[O6.40]

Nanofiltration membranes for ionic liquid recovery during pretreatment

A. Avram, X. Qian, S.R. Wickramasinghe*
University of Arkansas, USA

Ionic liquids could be an emerging solvent for pretreatment of lignocellulosic biomass. They act by dissolving the biomass which allows for much better access of the enzymes used for hydrolysis of cellulose. Further, ionic liquids reduce the crystallinity of the cellulose leading to higher glucose yields during enzymatic saccharification. The high cost of ionic liquids means that efficient recovery and recycle of the ionic liquid is essential for an economically viable process. Here, we investigate the feasibility of developing nanofiltration membranes for ionic liquid recovery.

We have created nanofiltration membranes with different barrier properties. Our aim is to maximize the ionic liquid recovered in the permeate while obtaining as high a rejection of saccharides as possible. Using base ultrafiltration membranes as a support structure, we have used interfacial polymerization (IP) to create a dense polyamide layer. Common reactive monomers are diamines such as piperazine (PIP), m-phenylenediamine (MDP) and p-phenylemediamine (PPD) and acid chloride monomers such as trimesoyl chloride (TMC), isophthaloyl chloride (IPC) and 5-isocyanato-isophthaloyl chloride (ICIC). Here we focus on the reaction of TMC with PIP. Recent publications highlight the ability to tune the performance of these nanofiltration membranes by inclusion of novel monomers as well as inorganic additives. Here we have incorporated 3-aminophenylboronic acid (BA) in the IP layer to control the sugar selectivity and permeance of the membrane. Membrane performance has been determined using feed streams consisting of aqueous saccharide solutions, water, ionic liquid and saccharide solutions as well as real biomass hydrolysates.

Keywords: interfacial polymerization, permeance, recovery, rejection

[O6.41]

Experimental assessment of osmotically assisted reverse osmosis for dewatering brines extracted from the geologic storage of carbon dioxide

J.T. Arena*[1], T.V. Bartholomew[2], M.S. Mauter[2], N.S. Siefert[1]

[1]US DOE National Energy Technology Laboratory, USA, [2]Carnegie Mellon University, USA

Reverse osmosis (RO) is at present the most efficient commercial technique to desalinate sea water; however, commercially-available RO membrane modules are unable to extract pure water from brines with salinities greater than ~90 g/L of total dissolved solids (TDS). This limitation has impeded the application of RO for dewatering brines having salinities >100 g/L TDS. Sources of these brines include those extracted during geologic CO□ storage (Figure 1) and those produced from hydrocarbon extraction.

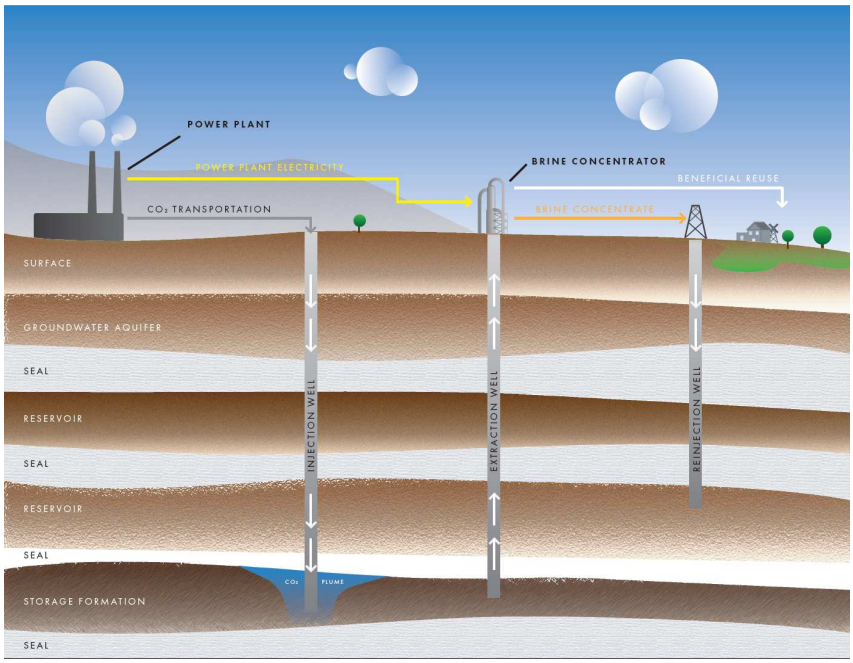


Figure 1 Schematic of a GCS operation where CO_2 is injected deep into the earth's subsurface where brine extraction is needed for formation pressure management.

The standard in high salinity brine concentration, using only electrical energy, is mechanical vapor compression (MVC). Compared to the efficiency of RO at 30-50%, MVC has an efficiency below 10%. Efficiency is the minimum theoretical work divided by actual work consumed. One potential alternative to MVC is the osmotically assisted reverse osmosis (OARO) process, shown in Figure 2. OARO operates by the dilution of a sweep solution on the permeate side of a membrane that is less saline than the feed. This lowers the osmotic pressure difference across the membrane, enabling dilution of the sweep using hydrostatic pressure to overcome the osmotic pressure difference. A subsequent OARO step can be used to regenerate the diluted sweep. Dilution of the sweep will continue in steps until its salinity is low enough salinity that it can be dewatered by conventional RO.

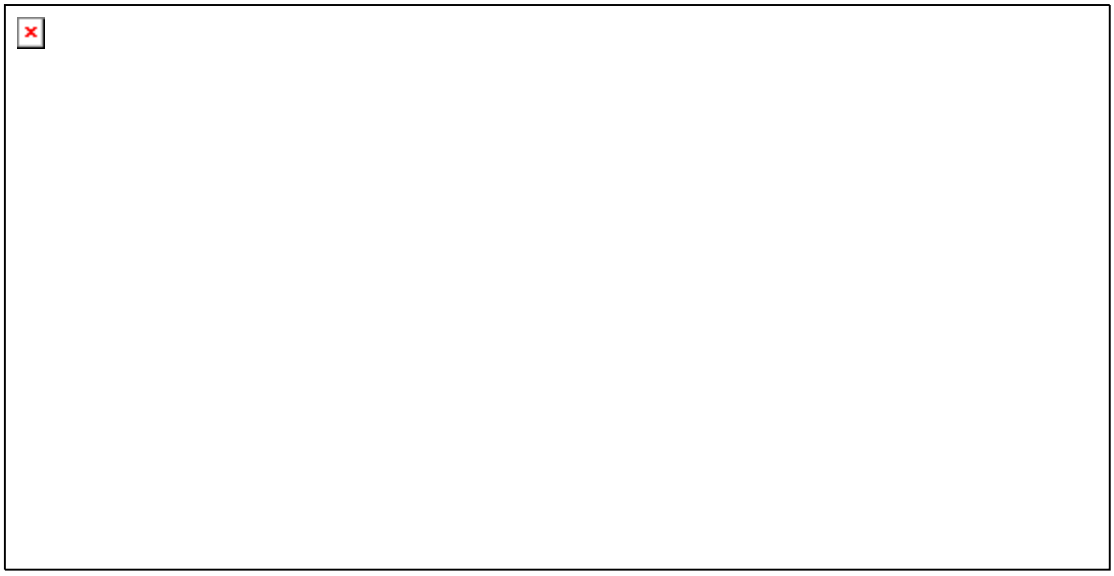


Figure 2 One possible configuration of a multi-stage OARO process to dewater a high salinity brine. Shown here are two OARO stages followed by the requisite final RO stages to produce a low salinity product.

Preliminary data, shown in Figure 3, has demonstrated the bench feasibility of OARO. Data from the bench testing will help develop a numerical fit of the membrane transport properties with respect to both feed and sweep solution salinity as well as the applied hydrostatic pressure for application to a system model. Some preliminary estimates on the energy requirements of OARO have shown that the OARO process is a more efficient approach for concentrating a high salinity brine compared to MVC.

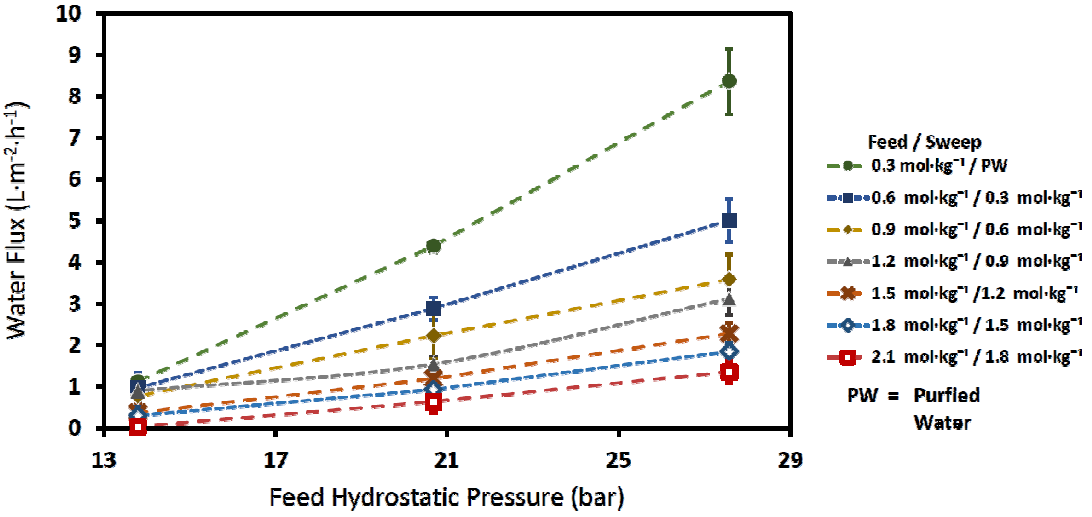


Figure 3 Experimental water flux in OARO for sodium chloride feed solutions of varying concentration at 25°C with a bulk concentration difference between the feed and sweep solutions of 0.3mol/$kg_{H□O}$. Water flux across the membrane occurs despite the high osmotic pressures of the feed solution due to a lower osmotic pressure difference across the membrane from the sweep solution on the permeate side of the membrane.

Keywords: high salinity brine, membrane transport, dewatering, reverse osmosis

[O6.42]

Concentration of downstream effluents from pharmaceutical industry using Aquaporin Inside ™ hollow fiber forward osmosis membranes - Influence of flow conditions on membrane performance

M.S. Camilleri-Rumbau*[1], L.C. Vargas[1,2], A. Romagnoli[3], K. Trzaskus[1], E. Gad[1], C. Hélix-Nielsen[2,4]

[1]Aquaporin A/S, Denmark, [2]Technical University of Denmark, Denmark, [3]GSK Vaccines S.r.l, Italy, [4]University of Maribor, Slovenia

In the vaccine industry, downstream processing is of extreme importance. Pharmaceutical downstream effluents are highly charged wastewater sources that can be concentrated. By means of aquaporin-based forward osmosis (FO) membranes in downstream operations, water reuse could be enhanced.

Aquaporin Inside ™ hollow fibre FO membrane module was used for concentration of ultrafiltration permeate from glycoconjugates-based fermentation broths. Several flow patterns applied on the feed solutions with varying cross-flow velocities with time (i.e. ramp-flow, peak-flow, step-wise flow) were investigated to study the effect of feed flow conditions on membrane fouling propensity. Additionally, the influence of dosing of concentrated draw solution to maintain a high osmotic pressure in the draw solution was investigated. Water tests were done before and after each fouling experiment. Basic-acidic chemical cleaning procedures were performed when J_w (water flux) after each fouling experiment was lower than the initial J_w. Feed and draw solution samples were taken for chemical analysis of total organic carbon (TOC), total nitrogen (TN), chemical oxygen demand (COD).

Results showed that the maximum J_p (permeate flux) values were obtained when applying peak-flow pattern on feed solutions with draw dosing. For all the fouling experiments, independently of the applied feed flow pattern, high chemical rejection was achieved (> 99.7% TOC, > 98.2% TN, > 90.0% COD rejection). However, the highest average chemical rejection was achieved when using stair-case flow pattern with dosing (i.e. 99.8%, 98.8% and 97.5% rejection of TOC, TN and COD, respectively). Permeate recovery was above 70% for all experiments. After 25 hours approximately of intermittent processing (i.e. fouling, water tests, cleaning, soaking, etc.), J_w decreased about 6%. Results thus indicated that FO is a feasible technique for concentration of downstream effluents from pharmaceutical industry.

Keywords: forward osmosis, pharmaceutical effluents, flow patterns, draw dosing

[O6.43]

Evaluation of fertilizer-drawn forward osmosis for sustainable agriculture and wastewater reuse in arid regions: From bench-scale performance to pilot-scale investigation on hydroponic lettuce

L. Chekli*[1], J.E. Kim[1], I. El Saliby[2], Y. Kim[1,3], S. Phuntsho[1], S. Li[4], N. Ghaffour[4], T. Leiknes[4], H.K. Shon[1]

[1]University of Technology Sydney, Australia, [2]Botanic Gardens and Centennial Parklands, Australia, [3]Korea University, Republic of Korea, [4]King Abdullah University of Science and Technology, Saudi Arabia

Wastewater reuse for irrigation of plants and crops has gradually become a common practice worldwide since it represents a viable alternative water source. However, wastewater effluent from a typical biologically treated effluent is generally not suitable for direct application due to the presence of pathogens (e.g. E-coli, faecal coliform, Giardia and Cryptosporidium, viruses etc.), organic and inorganic pollutants (e.g. heavy metals and micro pollutants) which are detrimental to both plants and human health. Therefore, advanced treatment process (e.g. membrane technologies) is essential to eliminate any health risks which are usually done using ultrafiltration (UF) or reverse osmosis or both.

This study investigated the sustainable reuse of wastewater using fertilizer drawn forward osmosis process through osmotic dilution of commercial nutrient solution for hydroponic application. Results from the bench-scale experiments showed that the commercial hydroponic nutrient solution exhibited similar performance (i.e. water flux and reverse salt flux) with other inorganic draw solutions (i.e. NaCl). The use of hydroponic solution provides all the required or balanced macro- and micronutrients in a single solution. Hydraulic cleaning effectively restored water flux up to 75% while osmotic backwashing restored by more than 95% illustrating the low-fouling potential of the FDFO process. Pilot-scale studies demonstrated that FDFO process is able to produce the required nutrient concentration and final water quality (i.e. pH and conductivity) suitable for hydroponic applications. Coupling FDFO with pressure assisted osmosis (PAO) in the later stages could help in saving operational costs (i.e. energy and membrane replacement costs). However, a trade-off between the process footprint and energy costs associated with the additional pressure needs to be further investigated to optimise this hybrid system. Finally, the test application of nutrient solution produced by the pilot FDFO process to hydroponic lettuce showed similar growth pattern as the control without any signs of toxicity or any mortality.

Keywords: Forward osmosis, Wastewater reuse, Hydroponics, Pilot-scale

[O6.44]

Combined forward osmosis-reverse osmosis for the treatment of brewery wastewater

C. Schneider*[1], A. Zarebska[1], C. Hélix-Nielsen[1,2]

[1]Technical University of Denmark, Denmark, [2]University of Maribor, Slovenia

Beer brewing is a water intensive process, using up to 12L of drinking water to produce 1L of beer. The bulk of this water leaves the brewing process as waste and has to be disposed of in a safe manner [1]. Increasingly strict governmental regulations render wastewater disposal a costly problem and raise interest for water recycling strategies.

Extracting reusable water from wastewater could help to lessen the costs by diminishing the wastewater volume while producing process water for cooling or cleaning.

Combined forward osmosis- reverse osmosis (FO-RO) has been shown to effectively retain pollutants while reducing energy input and fouling propensity compared to stand-alone RO [2][3].

Nevertheless, membrane fouling has to be taken into consideration. It is crucial to establish an efficient cleaning strategy in order to prolong membrane lifespan.

The objective of this study is to investigate the feasibility of water extraction from brewery wastewater in a pilot-scale FO-RO equipped with Hollow Fibre (HF) modules. Two types of brewery wastewater were used as a feed and 1M NaCl was used as a draw. FO and RO were run subsequently for 3,5h and 1h, respectively.

At the beginning and end of each experiment, the wastewater quality was analysed. Chemical cleaning was performed after every experiment, using NaOH followed by citric acid as cleaning agents.

Our preliminary findings indicate that brewery waste can be successfully treated by FO-RO and that the initial water flux can be largely recovered by chemical cleaning.

These results can contribute to finding novel ways of brewery wastewater treatment.

1. Kunze, W., T. et al,. Vol. 669. **1999**: Vlb Berlin,, Germany.

2. Cath, T.Y., et al., *J Memb Sci*, **2010**. 362(1–2): p. 417-426.

3. Lee, S., et al.. *J Memb Sci*, **2010**. 365(1): p. 34-39.

Keywords: forward osmosis, brewery wastewater, water extraction, cleaning

[O6.45]

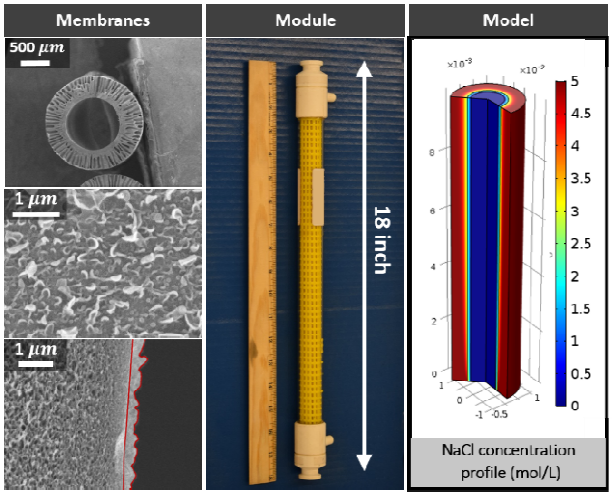
Optimizing hollow fiber membranes and modules for osmotic processes: From membranes to modules to models

J. Ren*, J.R. McCutcheon
University of Connecticut, USA

This study evaluates an approach to make thin film composite (TFC) hollow fiber membranes for forward osmosis (FO) by simply employing commercial ultrafiltration (UF) membranes as support material. A thin polyamide film with excellent selective properties was synthesized on the inner surface of hollow fibers via interfacial polymerization. Besides demonstrating good performance as TFC FO membrane supports, the commercial hollow fiber UF membranes also provide a systematic platform with consistent properties to study structure-performance relationship. A series of commercial UF membranes were used to evaluate how support layer surface pore size (MWCO) impacted the properties of the selective layer and overall performance of the TFC membranes.

Aside from using commercial hollow fibers as FO membrane supports at bench scale, we also demonstrate that the TFC hollow fiber FO membranes can be made on existing modules at pilot scale. A series of commercial modules with different fiber size were used to make TFC hollow fiber modules. The resultant modules were evaluated under various operating conditions. While we evaluate how performance was impacted by module operating conditions, overall the modules demonstrate impressive FO results.

With the availability of reproducible membranes and modules, we developed a computational fluid dynamics (CFD) model with COMSOL Multiphysics to optimize module design for FO application. The FO process in a hollow fiber membrane was simulated in a 2D axis-symmetry geometry and described by fluid dynamics coupled with mass transfer. We verified the model accuracy by constructing modules with the same dimensions and fibers and testing under pertinent conditions. The agreement between the simulation and experimental results provided insight into how independent variables would impact module performance. To allow our colleagues to take the advantage of this model, we also built it into an application and will release it for the community to use for free.



Keywords: forward osmosis, hollow fiber membrane, module design, property-performance relationship

[O6.46]

Tuning polymer dopes to boost the performance of outer-selective thin-film composite (TFC) hollow fiber membranes for osmotic power generation

Z.L. Cheng*[1], X. Li[2], Y. Feng[1], C.F. Wan[1], T.S. Chung[1]

[1]National University of Singapore, Singapore, [2]Wuhan University, China

The lack of effective membranes greatly hinders the use of pressure retarded osmosis (PRO) to harvest renewable osmotic energy. In comparison to the flat sheet and inner-selective hollow fiber configurations, the development of outer-selective hollow fiber membranes is much slower although it may be more attractive for real PRO applications. This study demonstrates that tuning the water content in polymer dopes can be an effective means to simultaneously enhance the mechanical robustness and water transport properties, boosting the PRO performance of outer-selective thin-film composite (TFC) hollow fiber membranes. Fundamental properties of polymer dopes with different water content and their influence on the hollow fiber supports as well as resultant TFC membranes were systematically investigated. With a low water content of 2 wt% in the polymer dope, the newly developed TFC membrane not only has the smallest structural parameter, highest toughness, and largest water permeability among all membranes studied but also displays an impressive peak power density of 10.05 W/m^2 at 22 bar using 1 M NaCl and DI water as feeds. To our best knowledge, this is the highest power density of outer-selective TFC PRO hollow fiber membranes reported in the literature. Mathematical models predict that approximately 25% performance increase can be further achieved if the external concentration polarization (ECP) effect is minimized. This study may provide useful insights to design high performance outer-selective TFC hollow fiber membranes for osmotic power generation.

Keywords: Pressure retarded osmosis (PRO), Thin-film composite (TFC), Outer-selective hollow fiber membrane, Water content in polymer dopes

[O6.47]

Optimizing operating parameters for minimum net energy consumption in a pilot-scale SWRO-PRO system

G. O'Toole*, A. Achilli
Humboldt State University, USA

Pressure retarded osmosis (PRO) is an emerging osmotic power technology that could mitigate the major challenges faced by seawater reverse osmosis desalination (SWRO): brine disposal and high energy consumption[i]. PRO generates power by using osmosis to "pump" water through a membrane from low concentration and low pressure to high concentration and high pressure. Current research on PRO has focused on optimizing power density (power generated per square meter of membrane) at the lab scale, and some theoretical research has sought to optimize operating conditions for net power density[ii]. Combining PRO with a SWRO system can generate up to 1 kWh per cubic meter of freshwater that is mixed with SWRO brine[i].

This study will determine the lowest net specific energy consumption (SEC_{net}) for producing fresh water from seawater in the first fully-integrated SWRO-PRO pilot-scale facility. The lowest SEC_{net} will be found by adjusting and testing six operating variables (**Error! Reference source not found.**). Each variable will be tested independently to narrow the range of optimal values. Within that narrow range, all possible combinations of variables will be tested to determine operating parameters for lowest SEC_{net}.

Physical system tests are currently underway. Modelled results (**Error! Reference source not found.**) indicate that SEC_{net} for a full facility decreases as the number of PRO modules increases. Additional modules increase both recovery and dilution, thereby generating more energy and diluting the brine before discharge. Additional modules also increase friction losses, decreasing recovered energy (Figure 1). Dilution and recovery are expected to be much lower in physical tests, causing friction losses to diminish a larger proportion of energy recovered by additional modules. By optimizing the SWRO-PRO system for minimum SEC_{net}, we aim to establish the current limit for PRO technology to recover energy from SWRO brine.

Table 1: Testing variables and ranges for optimizing the SWRO-PRO system SEC_{net}

	RO yield	PRO Dilution	PRO Recovery	PRO Pressure (bar)	PRO Feed Velocity (m/s)	PRO Draw Velocity (m/s)
Lower Range	0%	0%	0%	0	0.01	0.01
Upper Range	40%	40%	40%	20	0.20	0.20
Increment	5%	5%	5%	2	0.025	0.025
Total number of increments	8	8	8	10	8	8

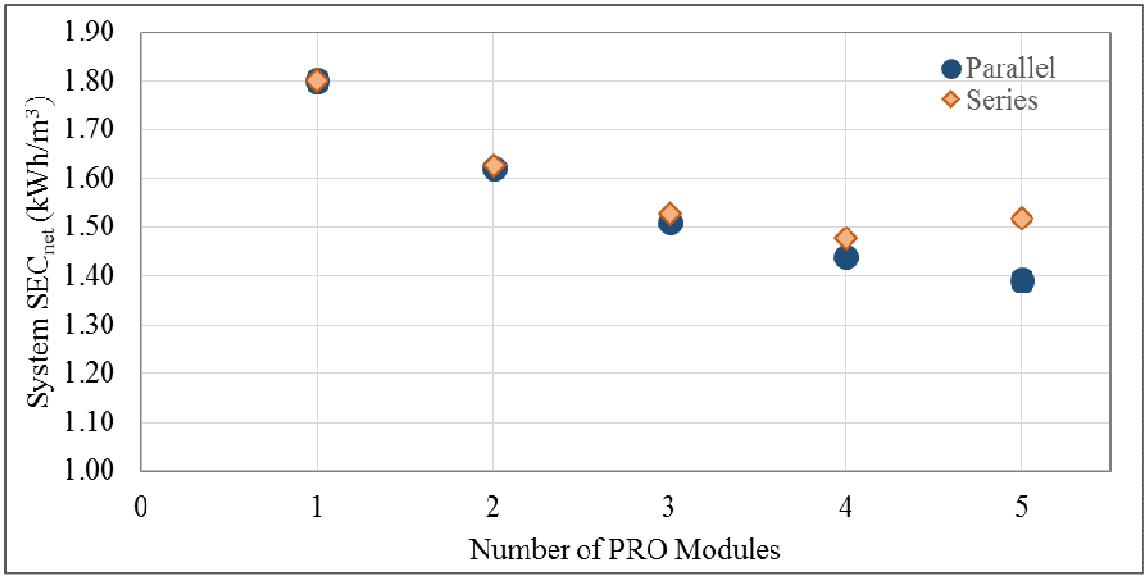


Figure 1: The SEC_{net} of the SWRO-PRO system is plotted versus the number of PRO modules. Increasing the number of PRO modules increases dilution and energy recovery for the series configuration until pressure losses overcome the energy recovery due to increased permeate. For the parallel configuration, increasing the number of PRO modules increases the energy recovery. For the modules-in-series configuration, pressure loss in the brine stream increases with increasing number of modules and reduces the energy recovery of the PRO system. For the modules-in-parallel configuration, pressure loss decreases with increasing number of modules and increases the energy recovery of the PRO system. For 1, 2 and 3 modules, the energy lost due to pressure drops in the series configuration is offset by increased permeate compared to the parallel configuration.

References:

[i] Achilli, A., Prante, J. L., Hancock, N. T., Maxwell, E. B., and Childress, A. E. 2014.

"Experimental Results from RO-PRO: A Next Generation System for Low-Energy Desalination." Environmental Science & Technology, 48, 6437-6443

[ii] Maisonneuve, LaFlamme, Pillay. 2016. "Experimental investigation of pressure retarded osmosis for renewable energy conversion: Towards increased net power." Applied Energy, 164, Pages 425–435

Keywords: desalination, pressure retarded osmosis, specific energy, energy recovery

[O6.48]

A pilot-scale module performance comparison in pressure-retarded osmosis

M. Yasukawa*, R. Horie, M. Shibuya, M. Higa

Yamaguchi University, Japan

Pressure-retarded osmosis (PRO) enables to convert salinity gradient power into electric power by using a semipermeable membrane. When using 1 m^3 of seawater as a higher concentration solution (draw solution: DS) and 1 m^3 of fresh water as a lower concentration solution (feed solution: FS), electric energy of about 0.5 kWh per 1m^3 per DS (or FS) can be potentially obtained. Although there are many studies to investigate and improve the PRO performance in lab-scale, a number of PRO studies in a pilot-scale is still few. To estimate the feasibility of PRO pilot plant, a pilot scale evaluation is indeed required instead of lab scale experiments. In this study, we evaluated the PRO module performances using 5 type modules (two hollow fiber (HF) modules and three spiral-wound (SW) modules) in a pilot-scale evaluation system.

5 types of PRO modules were evaluated using a pilot-scale PRO evaluation system. To investigate the steady stated module performance, we used PRO/RO hybrid system to keep a constant DS and FS inlet qualities. We investigated the effect of chemical and physical operating conditions such as DS concentration, inlet flow rate, applied pressure on the PRO performance of the modules, and then their module performances were compared each other from a view point of membrane area-based performance and module volume-based performance.

Preliminary pressure driven reverse osmosis (RO) experiments indicated SW membrane modules have higher water permeability than those of HF membrane module. Higher water permeability led hither water flux of SW modules under PRO operating condition, and therefore, membrane area-based performance of SW membrane modules was higher than those of HF membrane modules. However, because of much higher packing density of the HF modules, the volumetric-based performance of HF module was higher than those of SW module.

Keywords: Pressure-retarded osmosis, module operation, hollow fiber module, spiral wound module

[O6.49]

Advanced control system for batch membrane processes based on the boundary flux concept

M. Stoller*
University of Rome La Sapienza, Italy

Fouling on membranes appears to be one of the main technical limit of batch membrane technology. Sensible fouling of the membrane leads to a significant reduction of the performances, a decrease of the operating life and, as a consequence, economic unfeasibility of the process. Therefore, the adoption of fouling inhibition methods is strongly suggested.

Beside pretreatment processes and membrane characteristics, the operating conditions appears to be a key parameter to fouling inhibition. In this framework, the concept of the boundary flux assists to choose proper operating conditions where fouling is not triggered, and this work will cover a novel approach of design and development of an advanced control system, that relies on this concept and automatically allows to limit fouling formation during operation.

The developed control system is of inferential type, validated by experimental data and the use of a simulation software (HYSYS, Figure 1). In HYSYS, a custom made module simulating the membrane process and including the boundary flux equations was developed for the first time.

One of the main difficulties of this strategy is that the boundary flux is a function of the feedstock characteristics and time: both parameters are therefore not constant during batch operations. The success of the strategy relies therefore on the possibility to perform proper calculations and predictions in order to correctly follow the evolution as a function of the process operation time. The control system reads the input data (key parameters), perform the proper calculations on the evolution of the feedstock characteristics, check periodically the correctness of these predictions and according to this, evaluates the actual boundary flux value and the proper operating conditions to avoid sensible fouling. This permits to maintain a constant permeate flux during the whole operation without exceeding the boundary flux and thus trigger severe fouling conditions, but, compared to fixed set-point controllers, permits real time and before every start-of-operation adjustment, if required (Figure 2).

The use of this technique permits in case of a membrane treatment process of olive vegetation wastewater streams by ultrafiltration and nanofiltration membranes to suffer a pure water permeate loss only of about 10% in 6 years, compared to zero flux conditions reached within 10-12 days if no strategy is applied.

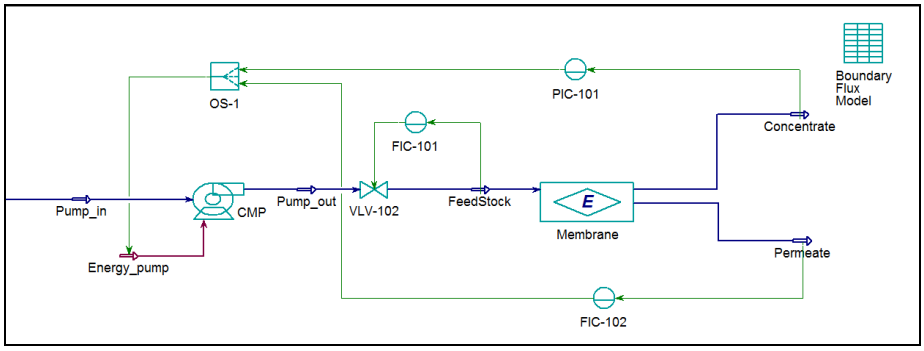


Figure 1: Scheme of the membrane process implemented in HYSYS

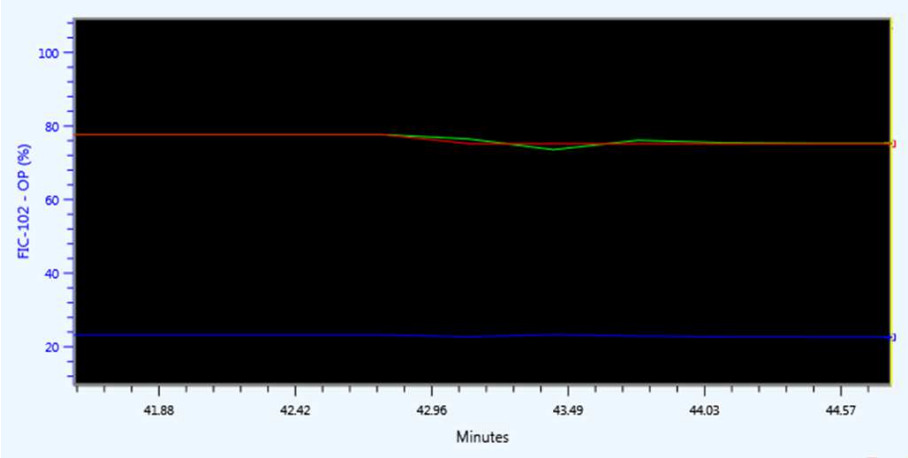


Figure 2: Permeate flux control at a constant value by the implemented control system

Keywords: Control system, Boundary flux, Fouling, Inferential model

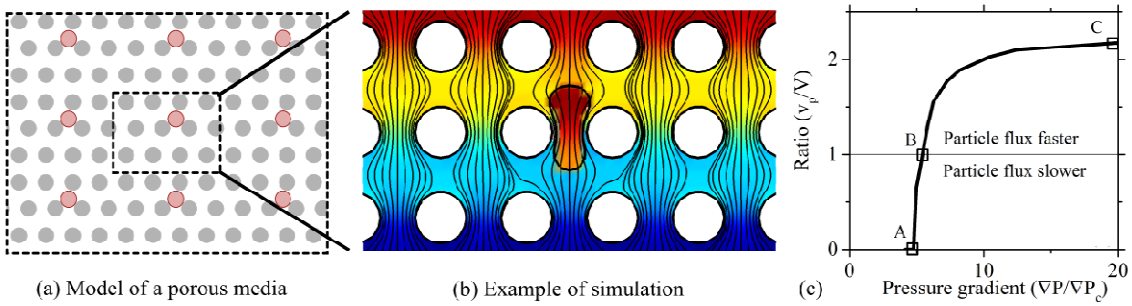
[O6.50]

The porous media effect in the permeation of soft vesicles

E. Benet, J. Pellegrino*, F.J. Vernerey

Univeristy of Colorado, USA

To improve the design of membranes aimed to separate or fractionate deformable particles (such as emulsions, vesicles, or oil-water suspensions), we have developed a multiscale approach that correlates the transport of the particles to various effects at different length scales: microscopic pore design, vesicle properties, and bulk flow within the porous media. The focus in this paper is on the scaling relationship between the particle's deformable properties (surface tension), the geometry of the system (pore shape and connectivity), and the overall vesicle's sieving through a periodic domain. At the microscale, the problem is studied using the extended finite element method to describe the creeping flow and vesicle transport inside a portion of a filtration membrane (Figs. a-b). The problem is then parameterized to build a larger scale simulation of a porous network where the interactions of multiple deformable particles is studied.



(a) Model of a porous media (b) Example of simulation (c)

The porous media is idealized here by a periodic distribution of circular obstacles (Fig a), and the results are presented as the relationship between the velocity of the particles (v_p) in this domain, and the overall pressure gradient applied on the membrane. These magnitudes are normalized with the average fluid velocity (V) and the minimum pressure required to cross a single pore, which is determined using a semi-analytical approach. Our model predicts that the applied trans-domain pressure gradient is not the same gradient experienced by each drop to deform and pass between obstacles (a pore throat), which is the one determining the vesicle's permeation capabilities. Using a parametric study, we show how these magnitudes are related to both obstacle size and distribution (tortuosity), the vesicle size and deformability, and the presence of other vesicles in the system affecting the fluid flow. These cases can provide a set of scaling rules to guide membrane design for droplet separations purposes.

Keywords: colloids, depth filtration, immiscible droplets, modeling

[O6.51]

Shear stress induced by spherical cap bubble rising in Newtonian and non-Newtonian liquids in immersed hollow fiber membrane systems

E. Radaei, X. Liu*, Y. Wang, G. Leslie, F. Trujillo

University of New South Wales, Australia

Recently, pulse bubble aeration have been used in immersed membrane systems exhibiting enhanced efficiency in fouling removal compared to coarse bubbles. However, the shear stress induced by pulse bubbles in non-Newtonian flow is unclear due to the lack of reliable measurement techniques and modelling limitations. In this study, a new three-dimensional CFD model was developed using ANSYS FLUENT to study the shear stress on industrial scale hollow fibers in non-Newtonian flow and compared with water flow.

The model was built on a pilot-scale membrane tank configured with five 1.5m long hollow fiber membranes. 100-200 ml spherical cap bubbles under various frequencies ranging from 0.3 to 0.5 Hz were sparged into a 0.5g/L xanthan gum solution in the tank. The rheological behaviour of the solution is comparable to 5.0g/L activated sludge collected from a MBR in North Head WTP (Manly, Australia) and incorporated into CFD modelling using an Ostwale-de Waele rheology model. The Volume of Fluid method was coupled with Realizable k – ε turbulent model to simulate the transient behaviour of the cap bubble in the air-liquid two-phase flow. Validation experiments were assessed in the same membrane tank by monitoring the bubble velocity via a camera and strain rate at the membrane surface by strain gauge.

The results indicate that the shear stress distribution is highly dependent on the fiber position and distance to bubble flow. The maximum shear stress was found 3.0Pa in water flow and 4.7Pa in non-Newtonian flow (Fig. 1). Furthermore, shear fluctuations, which are considered to be beneficial for the cleaning of membranes, were less pronounced for non-Newtonian fluid compared to shear fluctuations in water. Therefore, shear stresses are significantly influenced by rheology supporting recent findings that studies conducted in water cannot be transferred to MBRs.

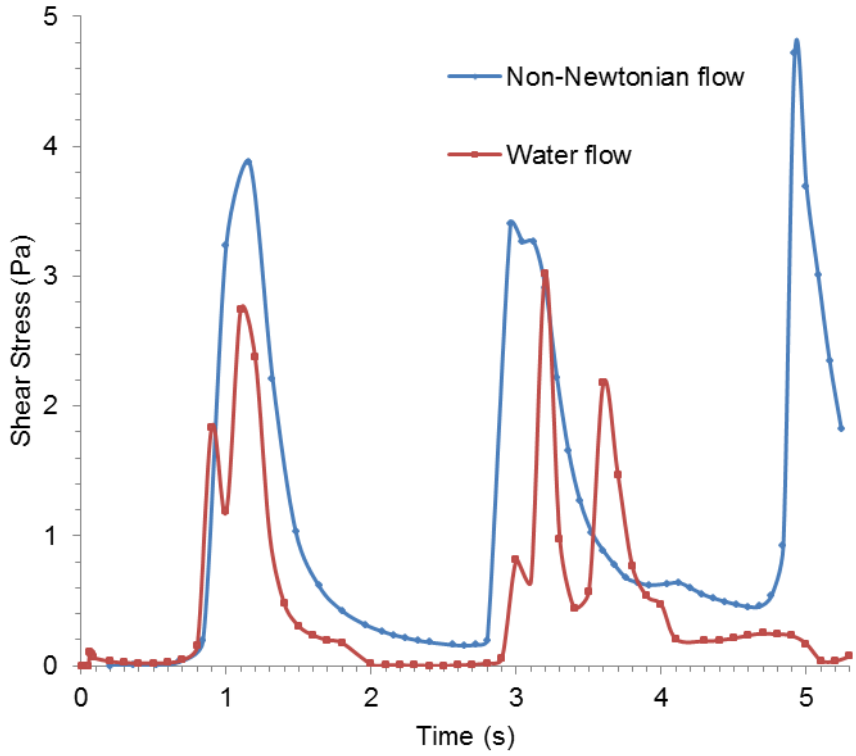


Fig. 1- Shear stress distribution in water and non-Newtonian flow

Keywords: Computational fluid dynamics, Spherical cap bubble, Non-Newtonian flow, Shear stress

[P2.101]

Molecular modelling of reverse osmosis using zeolite membranes for separation of hydrocarbon mixture

H. Takaba*, H. Ishihara
Kogakuin University, Japan

Separation of hydrocarbon mixtures is important processe in petrochemical industries and currently performed by the distillation with large energy consumption. Reverse osmosis using membranes is expected to be one of the alternative to the distillation because it has potential to reduce the energy consumption as well as the unit size with simple unit operation. In this paper, we present the molecular simulation study on reverse osmosis zeolite membranes for separation of hydrocarbon mixtures to predict the separation performance. To our knowledge, this study is first attempt to investigate the ideal performance of reverse osmosis zeolite membranes for hydrocarbon mixtures.

To model the reverse osmosis membrane, we constructed the structures of thin FAU type zeolite membranes including Ag^+ or Na^+ or no cations to investigate the effect of cations on separation performance for benzene/cyclohexane mixture. We carried out a non-equilibrium molecular dynamics where the reverse osmosis is achieved by applying the different pressure for both sides of unit cell those were controlled based on our suggested fluctuating wall method. We applied 200 atom to the feed side and the permeate side was controlled to maintain 1 atm.

The solvent molecules in the feed side transported to permeate side was successfully demonstrated. Ag-Y membrane showed the high flux and selectivity of about 2 for benzene, whereas high silica FAU membrane showed the cyclohexane selectivity with medium flux. Na-Y membranes showed a little benzene selectivity after equilibrium although in the beginning stage of separation it showed cyclohexane selectivity. Our simulation results indicate that separation performance significantly depends on the counter cation species. Out presented methods will be useful to predict the performance of zeolite membranes on reverse osmosis where both adsorption and diffusion determine the membranes performance.

Keywords: r everse osmosis, non-equilibrium molecular dynamics, hydrocarbon mixture, zeolite membranes

[O6.53]

Microporous vs dense materials for membrane distillation process: A critical analysis

D. Mejia*, E. Favre, C. Castel, C. Lemaitre

Laboratoire Réactions et Génie de Procédés, France

Membrane distillation is a promising technology for water desalination. However, commonly used porous hydrophobic membranes can get wetted, limiting the performance of the process. This study proposes the use of dense membranes as an alternative to avoid pore wetting and provides a guideline for the design of a high-performance dense membrane module for MD. The use of a dense layer has proven to be very effective at avoiding wetting in other membrane processes where this phenomenon is also limiting [1],[2].

Firstly, the performance of the dense and porous membranes was compared in terms of mass and heat transfer under the same operating conditions. Coupled mass and heat transfer equations were solved using a model developed in Matlab which was validated experimentally Fig 1. Both kind of membranes were compared in terms of pure water recovery and energy efficiency. Secondly, a sensitivity analysis was performed. The parameters evaluated were the permeability, which depends of the materials, the thickness, and the conductivity or insulating power of the dense membrane. Finally, the aforementioned parameters were optimized for the dense membrane. The conjunction of these parameters will determine the performance of the MD module. A thicker membrane will give a better insulation, thus better thermal efficiency but at the expense of higher mass transfer resistance and vice versa.

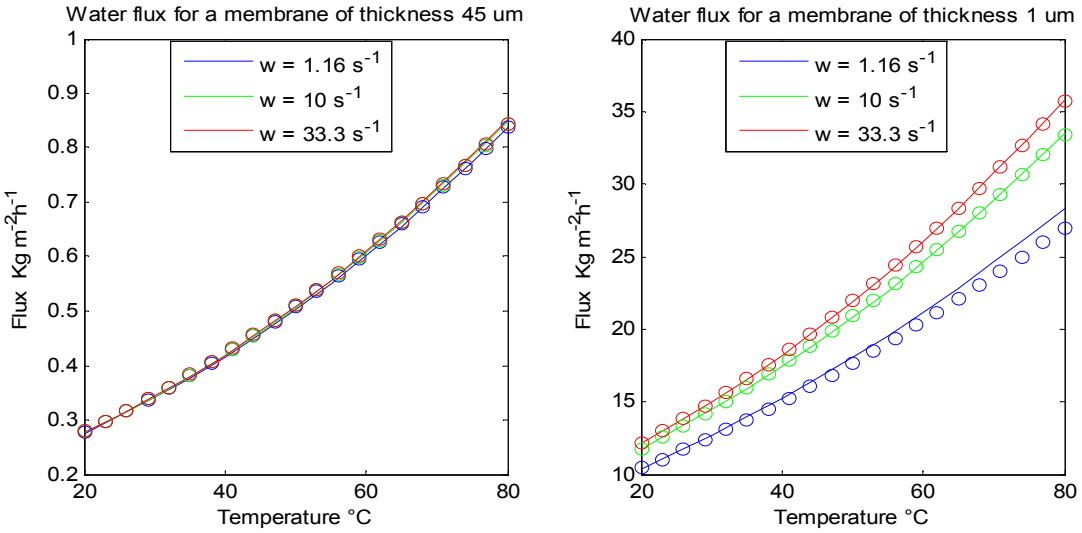


Figure.1. Water flux for two membrane thickness at various temperatures. (—) Simulated data (o) Experimental data.

The best configuration maximizing the energy efficiency and water recovery was found with the advantage of completely avoiding wetting in long term operation; main drawback of membrane distillation processes. Several dense materials and maximal membrane thicknesses that allow the same performance as a non-wetted porous membrane are proposed.

[1] B. Belaissaoui (2016) J.Membr.Sci, 513, 236–249.

[2] P.T. Nguyen, (2011) J.Membr.Sci. 377, 261–272.

Keywords: Intensification, membrane distillation, modeling, Parametric anamysis

[O6.54]

Numerical study on the formation mechanism of ultrafiltration polymeric membranes produced by the NIPS method

K. Yano*, K. Yoshimoto, T. Taniguchi, M. Ohshima
Kyoto University, Japan

Introduction:

Recently, some phase-field simulations have been conducted to provide insights into the formation mechanism of polymeric membranes produced by the non-solvent induced phase separation (NIPS) method. However, the final pore shape predicted in those simulations tends to be circular/spherical and to be isolated rather than continuous, due to the lack of rheological description of the polymer. Here we develop a new phase-separation model that can distinguish the polymer from the other liquid components by including the polymer's viscoelasticity.

Methods:

The volume fractions of non-solvent, solvent and polymer are assigned in each gridded space. In this study, we also introduce the so-called conformation tensor, W, which represents the local deformation of polymer chains. The time evolution of W is determined by an equation of motion that includes the polymer velocity and relaxation time. The polymer velocity is calculated from the equation derived from the three-fluid model which includes the polymer elastic moduli.

Results:

Figure 1 shows the time evolution of polymer volume fraction in the NIPS process. In case that the polymer is a viscous liquid (Fig. 1a), which is a typical setting for the phase-field simulations, the non-solvent-rich domains (i.e., pores) rapidly become circular in shape and gradually merge into large circles. In contrast, the viscoelastic case (Fig. 1b) demonstrates that the non-solvent-rich domains exist in the polymer network and remain irregular over a long course of simulation time.

Discussion:

The main reason for the large difference in pore structures is that in the viscoelastic case (Fig. 1b), the polymer resists being deformed by the phase-separation and interfacial forces. Remarkably, the final morphology obtained from our viscoelastic model captures some important characteristics of the real NIPS membranes, e.g., network structure of the polymer, irregular shape and distribution of the pores.

(291 words)

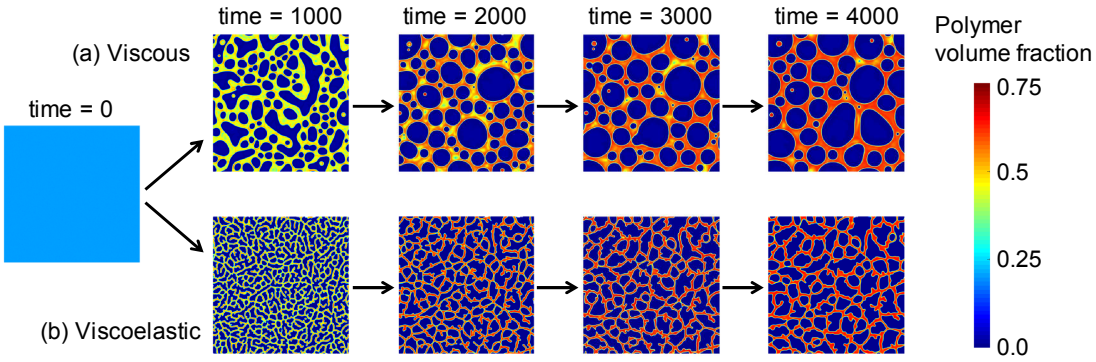


Fig.1 Time evolution of the membrane formation by the NIPS method: polymer treated (a) as a viscous liquid (i.e., conventional phase-field approach) and (b) as a combination of viscous liquid and elastic solid (i.e., proposed in this study)

Keywords: NIPS, viscoelastic model, dynamic simulation, membrane morphology

[O6.55]

Numerical and experimental study on a crossflow filtration module based on chaotic advection

T.G. Kang*[1], S.Y. Jung[2], K.H. Ahn[2], K.T. Park[3], S.U. Kim[3]

[1]Korea Aerospace University, Republic of Korea, [2]Seoul National University, Republic of Korea, [3]BKT Co. Inc., Republic of Korea

In a filtration module, progressive fouling on a membrane surface by the rejected particles results in the decrease in the effective pore size and the blockage of the membrane pores, which ultimately causes the decline in the permeate flux with time. Though applying high shear rate on the membrane surface delays the progress of fouling and can be an option to increase permeate flux in cross-flow filtration, it requires more energy to drive a pump. As an alternative, we propose a crossflow filtration module utilizing chaotic advection. Chaotic advection refers to a kinematical phenomenon in which the motion of fluid particles is chaotic in the Lagrangian sense even though the velocity field is simple in the Eulerian viewpoint. Thin plates with slanted barriers are periodically inserted in a tubular membrane module, creating spatially periodic two rotational flows with crossing streamlines. Such a flow portrait can induce chaotic advection, showing chaotic trajectory of fluid particles and uniformly distributing solid particles suspended in the fluid. To validate the feasibility of the proposed filtration module, we conducted numerical simulations and experimental studies on the membrane module. A numerical scheme combining the finite element and a particle-tracking method is employed to solve the flow problem. At a properly chosen set of geometrical parameters, fluid particles exhibit chaotic trajectories, even in laminar flows. The performance of the newly proposed membrane module is assessed by experimentation. The filtration performance of the membrane module with inserts is found to be the best compared with that of a tubular membrane module without inserts. It turned out that the membrane module utilizing chaotic advection is a practically attractive way to realize an efficient filtration system, minimizing the progress of fouling and enhancing the permeated flux.

Keywords: crossflow filtration, chaotic advection, numerical simulation, modeling

[O6.56]

Water transport through nanotubes: The effects of roughness and hydrophilicity of tube wall

W. Cao*[1], L. Huang[3], M. Ma[1], L. Lu[2], X. Lu[2]

[1]Tsinghua University, China, [2]Nanjing Tech University, China, [3]University of Oklahoma, USA

Membranes made from nanomaterials such as carbon nanotubes (CNTs) and graphene have been suggested to have a range of applications in water filtration and desalination.[1] Water transport through CNTs was found to be ultra-fast, especially in CNTs with a diameter of less than 2 nm. The tube surface chemistry and geometry can influence the water diffusion in nanotubes. The interaction strength between water molecules and the wall of a nanotube, characterized by the Lennard-Jones potential well depth, was been shown to have a significant impact on the ability for water molecules to transport through a nanotube.[2] Very few researchers have focused on both the effects of roughness and hydrophilicity of nanotube membranes.

In this work, the effect of wall roughness on the transport of water molecules in modified carbon nanotubes was investigated by using NEMD simulations. The hydrophilicity was obtained by changing the interaction between water and nanotubes. A nanotube whose surface was modified with a sinusoidal morphology is employed to mimic an “idealized” rough pore. The pressure was set to 200 MPa. Simulation results show that the water flux first increases and then decreases a little as the tube-water interaction increases for all the studied rough nanotubes. A sudden change of water flux was also demonstrated, when the ratio between the amplitude and wavelength of roughness change from 0.02 to 0.03. The variation value for hydrophobic nanotubes is smaller. The molecular mechanism was elucidated through the study of the radial density profile and hydrogen bonds.

References

(1) Werber, J. R.; Osuji, C. O.; Elimelech, M. Materials for next-generation desalination and water purification membranes. Nat. Rev. Mater. 2016, 1, 16018.

(2) Melillo, M.; Zhu, F.; Snyder, M. A.; Mittal, J. Water transport through nanotubes with varying interaction strength between tube wall and water. J. Phys. Chem. Lett. 2011, 2(23): 2978-2983.

[O7.01]

Stimuli-responsive polymer-based ultrafiltration membranes

M. Ulbricht*, M. Gajda, X. Lin

Universität Duisburg-Essen, Germany

There is rapidly increasing interest in stimuli-responsive materials, e.g., for controlled drug release or sensing applications. Very versatile are stimuli-responsive polymers which show large and reversible changes of degree of swelling as function of conditions such as temperature, pH value, etc. Even more interesting are systems where external physical stimuli, e.g., magnetic fields, can trigger the response, in particular membrane barrier properties. Different routes will be discussed with focus on materials where the separation selectivity for target molecules or particles in the ultrafiltration size range (2 to 50 nm) can be switched on demand. Using track-etched polymer membranes, the functionality of various stimuli-responsive polymers in different architectures within pores can be evaluated. By surface-initiated atom transfer polymerization (SI-ATRP) it is possible to tailor pore functionality by controlling grafting density, chain length and functional block sequence; solute size-selectivity and its switchability can be tuned by SI-ATRP conditions [1]. Reactive pore-filling with a hydrogel of tailored mesh size via *in situ* cross-linking polymerization is an alternative approach, and by integration of (super)paramagnetic nanoparticles as local "nanoheaters" it is possible to control membrane permeability and macromolecule sieving via "remote control" [2]. An easily scalable preparation route via phase separation of polymer-based blends toward such polymer-based nanohybrid membranes, leading to ultrafiltration selectivity that can be largely and fully reversibly switched "off" and "on" by an external high frequency electromagnetic, field will also be demonstrated (Fig. 1) [3]. Ongoing work is devoted to extensions and combinations of above mentioned concepts in order to further improve the versatility of the functional polymer-based membrane systems.

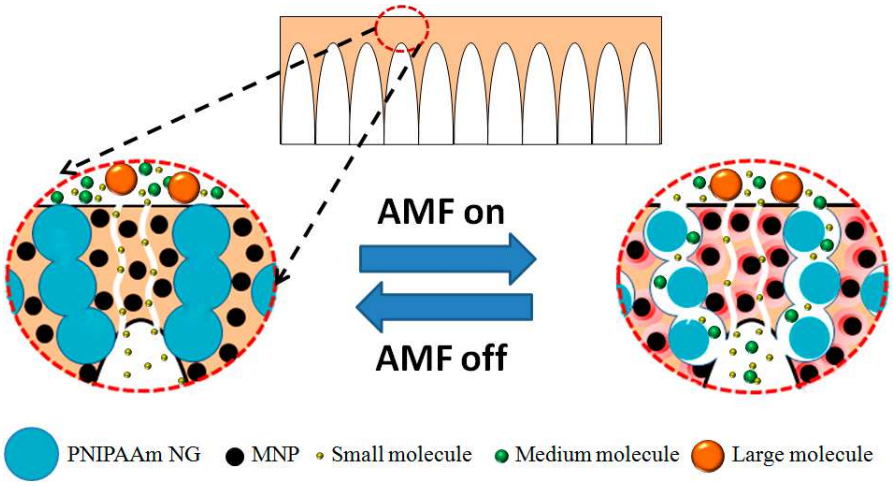


Fig. 1. Schematic illustration of anisotropic magneto-responsive polyethersulfone (PES)-based iron oxide nanoparticle (MNP) *cum* temperature-responsive hydrogel particle (PNIPAAm NG) mixed matrix composite ultrafiltration membrane: reversible change of molecule sieving through thin porous barrier layer with NG gates which are immobilized in PES macropores, by "remote control" triggering of nearby "nanoheaters" with alternating magnetic field (AMF).

[1] M. Gajda, M. Ulbricht, *J. Membr. Sci.* **2016**, *514*, 510.

[2] X. Lin, R. Huang, M. Ulbricht, *J. Mater. Chem. B* **2016**, *4*, 867.

[3] X. Lin, B. Nguyen Quoc, M. Ulbricht, *ACS Appl. Mater. Interf.* **2016**, *8*, 29001.

Keywords: Ultrafiltration membrane, Magneto-responsive, Temperature-responsive, Salt-responsive

[O7.02]

Smart membranes by interfacial polymerization of cyclodextrin-based supramolecular complexes

T. Huang*, L.F. Villalobos, K-V. Peinemann

King Abdullah University of Science and Technology, Saudi Arabia

Design and preparation of membranes with tunable and highly selective separation properties is of great interest and significance for numerous applications. In this work, we fabricated a novel type of thin film nanocomposite membranes by interfacial polymerization using cyclodextrin-based inclusion complexes as the aqueous reactant and a multifunctional acid chloride as the monomer in the organic phase. As far as we know this is the first work using supramolecular complexes as the monomer for thin film composite membrane fabrication. In one example we covalently bound parahydroxyazobenzene to α-cyclodextrin and used this compound for interfacial polymerization with trimesoylchloride on top of a mesoporous UF-membrane. A thin cross-linked cyclodextrin layer was obtained with pending azobenzene groups. It is well known that the light-responsive azobenzene can switch between cis- and trans conformation upon radiation. Only the trans configuration forms stable inclusion complexes with cyclodextrin. Depending on the radiation status the membrane has a more open structure (cis-form, no complex formation) or it is more dense (trans-form, higher degree of cross-linking due to complex formation). As a result, the membranes show water permeance changes under different irradiation conditions.

Not only the permeance is photo-switchable, but also the shape-selective selectivity. While in cis-form, azobenzene decomplex with cyclodextrin leaving the cavity of cyclodextrin for other molecules transportation. The crosslinking degree of membranes can be further controlled by using different cyclodextrins (α-cyclodextrin or β-cyclodextrin) as the host molecules.

Keywords: cyclodextrins, photo-switchable, Size-selective

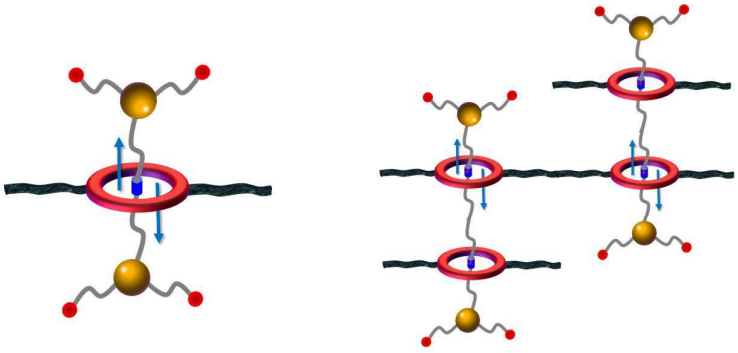
[O7.03]

Graft polyrotaxanes based ion shuttling membranes

X.L. Ge, Y.B. He, L. Wu*, T.W. Xu

University of Science and Technology of China, China

Highly permeable and selective ion-exchange membranes are desirable for ion separations and energy storage and conversion applications. Comb-shaped polyelectrolytes, in which ionic side chains covalent bound to hydrophobic main chains, have attracted significant attention in this respect owing to the self-assembly ability of ionic side chains to form continuous ions conducting channels. The higher content of ionic side chains is prefer to forming much more ordered channels, but in turn results in severe water swelling of ion conducting channels which therefore contribute less on ion conduction than expected. Here we report alternative graft polyrotaxanes based membranes that does not rely on the content of ionic side chains. The membrane has been synthesized by threading ionic linear guests into poly (crown ether) hosts via host-guest interaction. The thermally-trigged disruption of this interaction allows the shuttling of ionic side chains, which accelerates hydrated ions transport. The new concept of ion shuttling membrane has among the highest reported ion conductivity for polymeric membranes to date but much lower ionic content. Hence, this study may provide a new vehicle for improving the understanding of proton transport through hydrated polymer media, and will catalyze exploration of new applications of this novel class of polymers with a unique mode of ion transport.



(a) IEMs containing ion shuttles **(b) IEMs containing shuttling crosslinking networks**

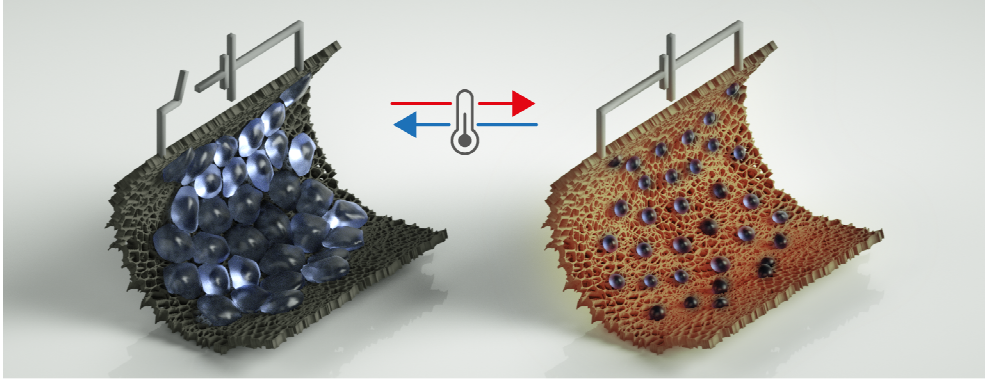
Keywords: Ion exchange membrane, Polyrotaxane, Ion transport, host-guest interaction

[O7.04]

Tuning permeability and selectivity of a heatable hollow fiber membrane with a thermo-responsive microgel coating

T. Lohaus*[1], P. de Wit[2], M. Kather[3], A. Pich[3], N.E. Benes[2], M. Wessling[1,3]

[1]RWTH Aachen University, Germany, [2]University of Twente, The Netherlands, [3]DWI – Leibniz Institute for interactive Materials, Germany



In recent years, research interest in stimuli-responsive materials to design membranes with tunable properties increased in order to customize membranes for adaptable process requirements. One of the most prevalent types of stimuli-responsive membranes uses temperature-sensitive microgels that change their size vastly in a short temperature range.

In the present work, we designed thermo-responsive membranes using an electrically conductive membrane composed of silicon carbide and carbon on which we immobilize thermo-responsive poly(N-vinylcaprolactam) (P-VCL) microgels. Immobilization of the microgels on the membrane was realized via filtration coating. By controlling the applied electrical power to the membrane, the temperature of the membrane can be directly adjusted and trigger responsiveness of permeability and selectivity. The present concept has advantages over existing tunable membranes. The membrane coating presents an effective and feasible way to functionalize membranes. The properties of the modified fiber can be tailored by the direct heating of the fibers independent of the feed temperature.

Scanning electron microscopy pictures show a uniform coating on the membrane surface and inside the pores. The microgel coating was tested to be stable without a loss in permeability for more than 30 days. Also, during backwash and backwash with heating, the modified membrane keeps a stable, switchable behaviour. Thermo-responsiveness remains reversible and stable in all conducted experiments. The controlled hydraulic resistance of the membrane behaves according to the hydrodynamic radius of the microgel. The retention of a 200kDa dextrane can be controlled in a range of 10-80% by heating the membrane from 20°C to 45°C.

Promising applications arise from the possibility of tuning membrane resistance without pausing operation. The variable permeability could be applied to filtration processes that are prone to fouling, with a more efficient cleaning cycle when backwashing at higher permeabilities, which might decrease the necessary cleaning duration while increasing cleaning results.

Keywords: Thermo-responsive P-VCL microgel, Heatable inorganic membrane, Stable and backwashable microgel coating, Tunable membrane resistance and retention

[O7.05]

Highly selective artificial K^+ channels within bilayer membranes

Y-M. Legrand*, A. Gilles, Z. Sun, I. Kocsis, M. Barboiu
Institut Europeen des Membranes CNRS/UM/ENSCM Montpellier, France

Introduction:

Natural K^+ channels such as KcsA conduct at **high rates** with an extraordinary **selectivity for K^+** cations, excluding the Na^+ or other cations. Biomimetic artificial channels using crownethers, cyclic peptides, barrel-stave superstructures, and bola-amphiphiles have been designed in order to **mimick the ionic activity of natural channels**, but simple artificial systems presenting high K^+/Na^+ selectivity are rare. Among these artificial systems, the macrocyclic crownethers have already been studied as ion-translocators in bilayer membranes and this project aims at taming artificial ion-channels formed by H-bonded stacks of crownethers derivatives, in which **K^+ conduction is highly preferred to Na^+ conduction**.

Methods:

15C5 and 18C6 crownwether bioconjugates with varying hydrophobic tales have been designed and tested for cation and transport activity using fluorescent and bilayer clamp assays. EYPC liposomes (LUV - 100 nm diameter), filled with a pH-sensitive dye (HPTS) and 100mM NaCl in buffer were suspended in phosphate buffer.

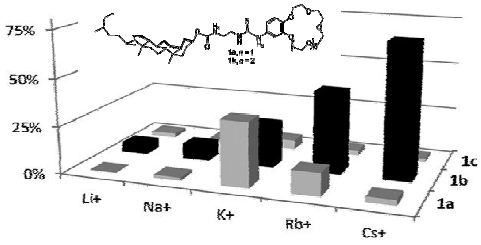
Results:

Self-aligned supra-channels

- Directed H-bonded networks forming cooperative ion channels.
- Media templating (even in competitive situation Na^+/K^+).
- Polar head selectivity (15C5 vs 18C6).
- Non-polar tail effect in bilayer incorporation (alkyl chain, cholesteryl, squaryl, etc).

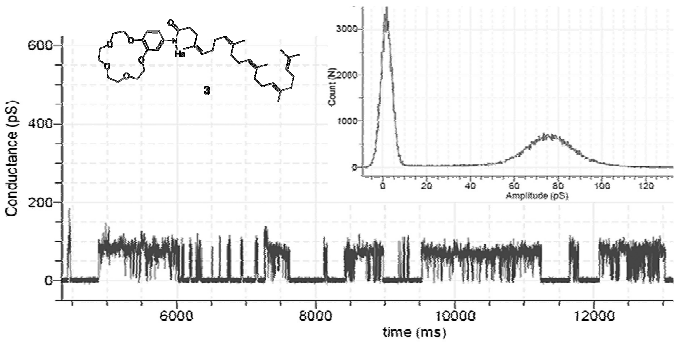
Crown Ether bioconjugates:*Fast & Selective*

- High kinetic selectivity (Na^+/K^+): $S_{K+/Na+}$~60
- High K^+ permeability : $k_K{}^+ = 87{,}5x10^{-3}\ s^{-1}$
- Multivalent recognition of K^+ by the crownether



Electrical gates

- Dynamic channel formation
- Single channel conductance : **C** = 75pS (SQ)
- Pore radius (SQ): $1Å < \mathbf{r}_P < 2Å$
- Anion/cation selectivity: $S_{Cl-/K+}$ ~3



Conclusion

- Evidences of synergistic adaptive behavior
- Dynamic self-instructed (“self-trained”) ion-channel systems
- High and unique performances (selectivity K^+/Na^+, permeability)
- Unprecedented cation driven constitutional polarization of the membrane
- Self-assembled simple bioconjugates are good competitors for synthetic ion-channels

References

Sun Z.; Gilles A., Kocsis I.; Legrand Y.-M.; Petit E.; Barboiu M. **Chem.Eur.J.,2016;22:2158**

Sun Z..; Barboiu M.; Legrand Y.-M.; Petit E.; Rotaru A. **Angew.Chem.Int.Ed.,2015;54:14473**

Gilles A., Barboiu M. **J.Am.Chem.Soc.,2016;138:426**

Keywords: synthetic ion channels, synergistic adaptive behavior, K+ selectivity, Dynamically self-instructed pores

[O7.06]

Controllable multicompartmental capsules with distinct cores and membranes for synergistic release

F. He*, W. Wang, M. Li, R. Xie, X.J. Ju, Z. Liu, L.Y. Chu
Sichuan University, China

Introduction: A facile and flexible approach is developed for controllable fabrication of novel multiple-compartmental calcium alginate capsule membranes from all-aqueous droplet templates with combined coextrusion minifluidic devices for isolated coencapsulation and synergistic release of diverse incompatible components.

Methods and Results: The multicompartmental capsules exhibit distinct compartments, each of which is covered by a distinct part of a heterogeneous membrane. The volume and number of multiple compartments can be well-controlled by adjusting flow rates and device numbers for isolated and optimized encapsulation of different components; while the composition of different part of the heterogeneous membrane can be individually tailored by changing the composition of droplet template for flexibly tuning the release behavior of each component. Two combined devices are first used to fabricate dual-compartmental capsule membranes, and then scaled up to fabricate more complex triple-compartmental capsule membranes for coencapsulation. The synergistic release properties are demonstrated by using dual-compartmental capsules which contain one-half membrane with constant release rate and the other half membrane with temperature-dependent release rate.

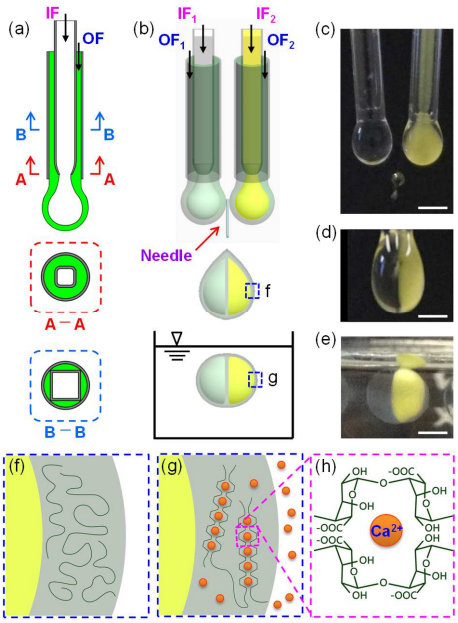


Figure 1. Coextrusion minifluidic devices for fabrication of dual-compartmental calcium alginate capsule membranes.

Discussion: Such a heterogeneous membrane provides more flexibilities for synergistic release with controllable release sequence and release rates to achieve advanced and optimized synergistic efficacy. The multicompartmental capsule membranes show high potential for applications such as drug codelivery, confined reactions, enzyme immobilizations, and cell cultures.

Keywords: Multicompartmental capsules, Distinct shell membranes, Calcium alginate, Coencapsulation

[O7.07]

Localized heat generation from magnetically responsive membranes

A. Vu*, Q. Yang, S.R. Wickramasinghe, X. Qian
University of Arkansas, USA

Commercial thin film composite nanofiltration NF270 and microfiltration polyethylene terephthalate (PET) track-etched membranes were modified by grafting thermo-responsive poly (N-isopropylacrylamide) (PNIPAM) polymers via surface initiated atom transfer radical polymerization (ATRP). The polymer chain ends were conjugated with super-paramagnetic (Fe_3O_4) nanoparticles. Each tailored super-paramagnetic nanoparticle acts as a nano-heater under an external oscillating magnetic field. The localized heat generated induces the lower critical solution temperature (LCST) transition for the PNIPAM in aqueous solution. The phase transition of the polymer leads to the alteration of membrane transport properties. Based on whether the modification occurs on the membrane surfaces or inside the membrane pores, localized heating affects membrane permeability differently for NF270 and PET membranes. Filtration of polystyrene latex particles through PET membranes demonstrates that it is possible to modulate the pore size by applying an external oscillating magnetic field.

Keywords: temperature responsive polymers, nanoheaters, surface modification, Magnetic nanoparticles

[O7.08]

Smart gating membranes with *in situ* assembled responsive nanogels as functional gates

L.Y. Chu*, F. Luo, R. Xie, Z. Liu, X.J. Ju, W. Wang
Sichuan University, China

Introduction: Smart gating membranes, inspired by the gating function of ion channels across cell membranes, are artificial membranes composed of non-responsive porous membrane substrates and responsive gates in the membrane pores that are able to dramatically regulate the trans-membrane transport of substances in response to environmental stimuli. Easy fabrication, high flux, significant response and strong mechanical strength are critical for the versatility of such smart gating membranes.

Methods: Here we show a novel and simple strategy for one-step fabrication of smart gating membranes with three-dimensionally interconnected networks of functional gates, by assembling responsive nanogels on membrane pore surfaces in situ during a vapor-induced phase separation process for membrane formation.

Results: The smart gating membranes with *in situ* assembled responsive nanogels as functional gates show large flux, significant response and excellent mechanical property simultaneously.

Discussion: Because of the easy fabrication method as well as the concurrent enhancement of flux, response and mechanical property, the proposed smart gating membranes will expand the scope of membrane applications, and provide ever better performances in their applications.

Keywords: smart gating membranes, nanogels, in situ assembly, responsive membranes

[O7.09]

Magneto-responsive membranes from self-assembly of block copolymers and iron oxide nanoparticles

D. Quemener*[1], L. Upadhyaya[1], M. Semsarilar[1], A. Deratani[1], R. Fernández-Pacheco[2], G. Martinez[2,3], R. Mallada[3], I. Coelhoso[4], C. Portugal[4], J. Crespo[4]

[1]Universite de Montpellier, France, [2]Networking Research Centre on Bioengineering, Biomaterials and Nanomedicine, Spain, [3]Aragon Nanoscience Institute, Spain, [4]Universidade Nova de Lisboa, Portugal

Block copolymers have emerged among the most promising precursors of ordered membranes due to the ease to reach a high degree of control in polymerization processes along with a large architectural diversity offered. In this work, block copolymers were co-assembled with iron oxide nanoparticles to promote magneto-responsivity to polymer membranes.

Block copolymer particles made of poly(methacrylic acid)-b-(methyl methacrylate)) (PMAA-PMMA) were synthesized using RAFT dispersion polymerization in ethanol at 70 °C. The PMAA block is soluble in ethanol and acts as a steric stabilizer for the growing insoluble PMMA chains, resulting in the in situ formation of diblock copolymer nano-objects (Polymerization Induced Self-Assembly (PISA)) in the form of spheres, worms or vesicles, depending on the precise reaction conditions as judged by transmission electron microscopy and dynamic light scattering studies. Two detailed phase diagrams using $PMAA_{27}$ and $PMAA_{47}$ macro-chain transfer agents were constructed as a road map for the synthesis of pure morphologies (Figure 1).

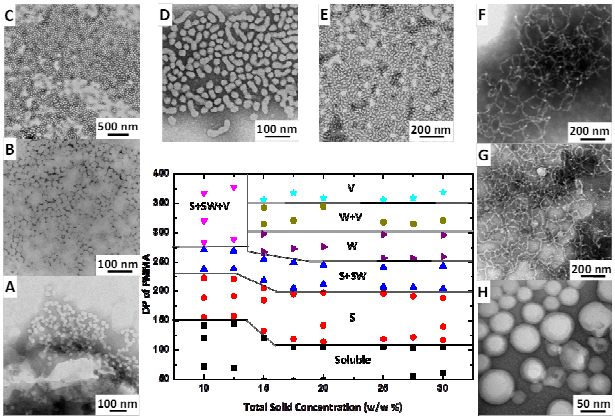


Figure 1. Example of phase diagram constructed for $PMAA_{47}$-$PMMA_Y$.

On the other side, the inorganic counterpart, iron oxide nanoparticles coated with poly(methacrylic acid)-b-poly(quaternized 2-(dimethylamino) ethyl methacrylate) were synthesized. The electrostatic co-assembly of iron oxide nanoparticles and diblock copolymer (unimers or nano-objects) enabled to prepare a series of magneto-responsive membranes (Figure 2).

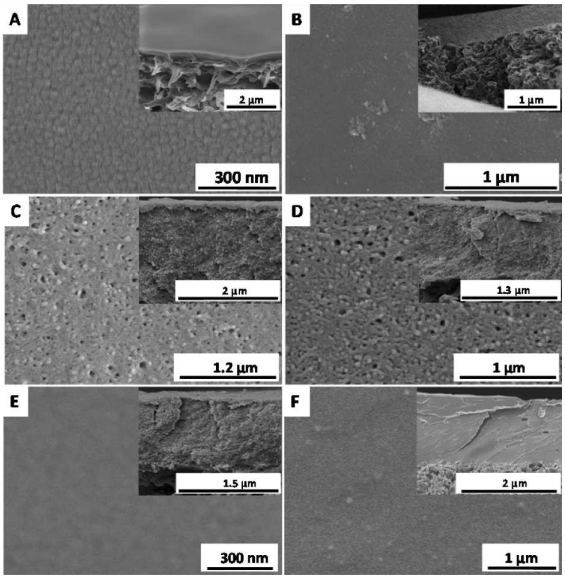


Figure 2. SEM images of film top surface with inscribed cross-section before and after filtration for membranes made out of spheres (A and B), worms (C and D), and vesicles (E and F) blended with iron oxide particles.

Under an external magnetic field (up to 1.15 T), the membrane water flux was found to increase by up to 30%. The AFM and STEM analysis suggest that the magnetic nanoparticles move within the membrane structure during application of the magnetic field. This displacement/rearrangement causes constant changes in the membrane structure and consequently on the membrane permeability.

Keywords: Block copolymer, self-assembly, magneto-responsive

[O7.10]

Optimising the in-filtration tunability of electrically responsive polyaniline membranes: Effect of dopant molecular weight and doping temperature

S. Shahid, A.K. Holda, D.A. Patterson, I. Amura*
University of Bath, UK

Pervaporation has become one of the most promising technologies for low energy recovery and purification of products from fermentation broths. Current organophilic pervaporation membranes however lack the required separation characteristics to be cost-effective. To help address this, new membranes incorporating selective phases are being developed. Here, the effect of MOF-synthesis solvent on the structures of copper MOFs with glutarate and 4,4'trimethylenedipyridine ligands is examined and how this effects mixed matrix membrane (MMM) pervaporation performance at different MOF loadings.

MOFs prepared in methanol (CuGluBpp-MeOH) and acetone (CuGluBpp-Acetone) differ in the orientation of the bipyridyl ligand within the framework exhibiting similar pore characteristics with differing crystal morphology, (Figure 1) which significantly affected pervaporation.

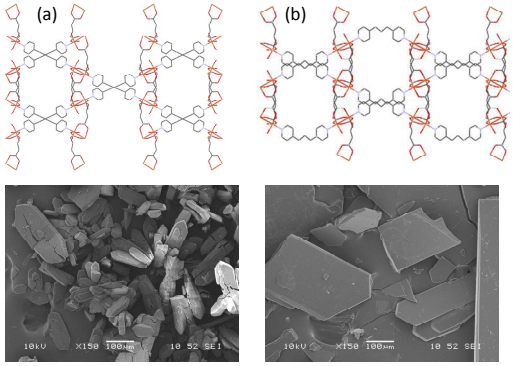


Figure 1. (a) CuGluBpp-Acetone and (b) CuGluBpp-MeOH (above) looking down the c-axis of the crystal structures, (below) SEM images showing the different crystal morphology.

Instead of the expected pore shape effects, crystal morphology dominated MMM selectivity. The CuGluBpp-MeOH exhibited plate-like crystals which due to the doctor blade casting process lay parallel to the membrane surface/perpendicular to permeate flow (identified through PXRD, SEM), producing poor flux and selectivity with increasing MOF wt% (Figure 2a). The CuGluBpp-Acetone had smaller, thicker crystals allowing a random orientation within their MMMs. This produced a superior separation with an optimum loading at 15 wt% of CuGluBpp-Acetone (Figure 2b) giving a pervaporation-separation-index of 567, 0.061 kg m^{-2} h^{-1} total flux and 10.3 separation factor for pervaporation of a 5 wt% acetone feed at 30 ºC. Total flux and separation factor of the 15 wt% loaded membrane increased with increasing temperature and acetone concentration.

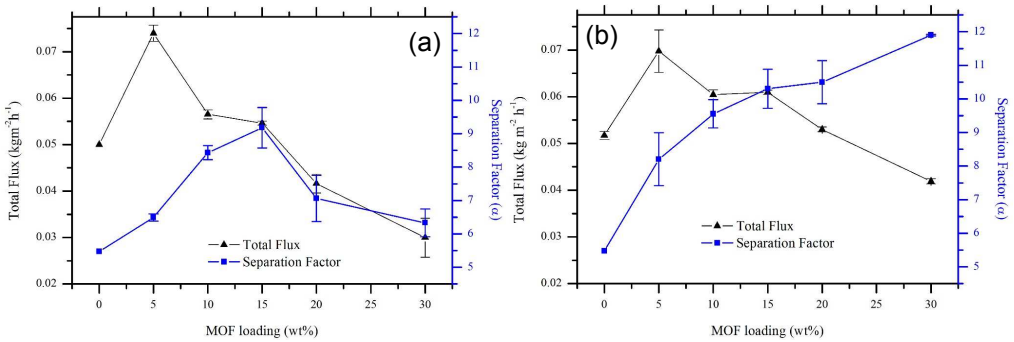


Figure 2. Pervaporation performance of (a) CuGluBpp-MeOH-MMM, (b) CuGluBpp-Acetone-MMM.

Overall, this study indicates that MOF synthesis solvent affects MOF structure and pore orientation, however it is the overall crystal structure of these MOFs that is the main influence on MMM pervaporative separation properties.

Keywords: Polyananiline, acid dopant, electrically tunable, ultrafiltration

[O7.11]

Development of a new pH and temperature responsive poly(N,N-(diethylamino)ethyl methacrylate) and pluronic F127 based thin film composite nanofiltration membrane

C. Bar*[1], M. Uz[2], N. Caglar[1], S.K. Mallapragada[2], S.A. Altinkaya[1]
[1]*Izmir Institute of Technology, Turkey,* [2]*Iowa State University, USA*

In this study, a new type of thin film composite nanofiltration (TFC NF) membrane was developed by using a pH and temperature responsive pentablock copolymer (PBC). The block copolymer was synthesized by atom transfer radical polymerization (Figure 1) and consists of temperature responsive Pluronic F127 (PEO-b-PPO-b-PEO) as middle block and pH responsive poly(N,N-(diethylamino)ethyl methacrylate) (PDEAEM) as end blocks [1].

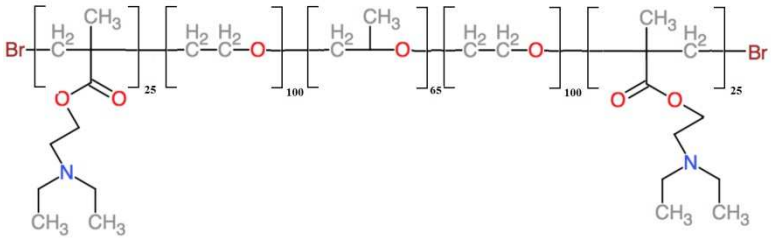


Figure 1. The structure of pentablock copolymer

The support membrane was prepared from polysulfone/sulfonated polyethersulfone through nonsolvent induced phase separation and the pentablock copolymer was attached through electrostatic interaction. The lower critical solution temperature of PPO block is 8°C and the PDEAEM block (pKa=7.6) shows a sharp pH-sensitive solubility behavior. In order to change the conformation of the chains from a highly hydrated expanded form to a collapsed hydrophobic state, the pH and temperature of feed solution were changed as pH=4, 7.6, 8.5 and T=4°C and 25°C, respectively. The influences of pH and temperature on the structure of the membrane were investigated with pure water flux measurements and the change in pore size quantified through determining rejection of model neutral solutes [polyethylene glycol (Mw=1000), raffinose (Mw=504), glucose (Mw=180) and glycerol (Mw=92)] by the membranes. The pore sizes were evaluated by combining experimentally measured rejection data with following equations [2,3].

$$R = 1 - \frac{C_p}{C_f} = 1 - \frac{K_{i,c}\Phi}{1-\exp(-Pe_m)[1-\Phi K_{i,c}]} \quad (1)$$

$$Pe_m = \frac{K_{i,c}}{K_{i,d}}\frac{VL}{D_{i,\infty}A} \qquad \Phi = (1-\lambda)^2 \qquad \lambda = \frac{r_s}{r_p} \quad (2)$$

$$K_{i,d} = K^{-1}(\lambda,0) \qquad K_{i,c} = (2-\Phi)G(\lambda,0) \quad (3)$$

$$K^{-1} = 1 - 2.401\lambda + 1.153\lambda^2 - 0.118\lambda^3 \quad (4)$$

$$G(\lambda,0) = 1 + 0.042\lambda - 0.941\lambda^2 + 0.339\lambda^3 \quad (5)$$

In these equations C_p and C_f represent the solute concentrations in permeate and feed streams, V is the filtration rate, L and A are the membrane thickness and area, $D_{i,\infty}$ is the solute diffusivity in solution, r_s and r_p are the solute and pore sizes. The membranes were further characterized with SEM, AFM, contact angle and zeta potential measurements. We demonstrated that PDEAEM- PEO-b-PPO-b-PEO- PDEAEM based TFC NF membranes can display distinct multi-responsive properties under different pH and temperature.

Acknowledgment

This study was supported by The Scientific and Technical Research Council of Turkey (TUBITAK, Grant Number: 115M464).

[1] Determan, M.D., Cox, J.P., Seifert, S., Thiyagarajan, P., Mallapragada, S.K. 2005. “Synthesis and characterization of temperature and pH-responsive pentablock copolymers”, Polymer, 46, 6933-6946.

[2] Deen, W.M. 1987. “Hindered transport of large molecules in liquid-filled pores”, AIChE Journal, 33, 1409-1425.

[3] Bowen, W.R., Mohammad, A.W. 1998. “Characterization and prediction of nanofiltration membrane performance-A general assessment”, I. Chem. E., 76, 885-893.

Keywords: poly(N,N-(diethylamino)ethyl methacrylate)/pluronic F127 pentablock copolymer, pH and temperature responsiveness, Nonsolvent induced phase separation, Thin film composite nanofiltration membrane

[O7.12]

Frequency dependent electrochemical stability of self heating carbon nanotube membranes: Implications for membrane distillation

D. Jassby*[1], A. Dudchenko[2]

[1]UC Riverside, USA, [2]Carnegie Mellon University, USA

Water shortages and brine waste management are an increasing challenge for coastal and inland regions, with high salinity brines (such as produced water or reverse osmosis waste brines) presenting a particularly challenging problem. These high-salinity waters require the use of thermally driven treatment processes, such as membrane distillation (MD), which suffer from high complexity and cost. Herein, we demonstrate how controlling the frequency of an applied alternating current at high potentials (20 Vpp) to a porous thin-film carbon nanotube (CNT)/polymer composite Joule heating element can prevent CNT degradation in ionizable environments such as high-salinity brines. Using electrical impedance spectroscopy, we show that electrooxidation of CNTs is a strong function of the applied frequency and ion concentrations in the CNT's immediate environment. At high frequencies (>100 Hz) electrons can only charge the electrical double layer (EDL), while at low frequencies electrons in the fully charged EDL can participate in CNT-degrading electrochemical reactions. By operating at sufficiently high frequencies, these porous thin-films can be directly immersed in highly-ionizable environments and used as self-heating flow-though heating elements. Finally, we demonstrate that porous CNT/polymer composites can be used as a self-heating membranes for desalination. These self-heating membranes are used to directly heat high salinity brines at the water/vapor interface of the MD element, making it possible to achieve exceptionally high single-pass recoveries that approach 100%, far exceeding the classical MD theoretical limit of 6.5%.

Keywords: Self heating membranes, Membrane distillation, Conducting membranes, Electrochemistry

[O7.13]

Synthesis scale up of high performance RO and uf membranes with responsive hydrophilic brush layers

S. Kim, J. Zhang*, A. Rahardianto, Y. Cohen
University of California, USA

Tethered hydrophilic polymer brush layers that are responsive to salinity and pH changes have been touted as being an effective means for reducing membrane fouling while also enabling effective cleaning without resorting to the use of chemical cleaning agents. Such polymer brush layers can swell depending on salinity or pH levels and thus the membrane surface can be made to responsive. In the present work, tethered poly(acrylic acid) brush layers were synthesized onto polyamide (PA) reverse osmosis (RO) and polysulfone (PSf) ultrafiltration (UF) membranes of a pre-selected (i.e., tailored) permeability. These surface-structured membranes were fabricated in the form of large sheets suitable for assembling spiral-wound membrane elements. Synthesis of the responsive brush layer was achieved via surface activation with atmospheric pressure plasma (APP), followed by free-radical graft polymerization. Once the APP process and subsequent surface graft polymerization were optimized (e.g., with respect to plasma precursor gas, treatment time, initial monomer concentration, temperature and reaction time) the presence of the polymer brush layer was confirmed via X-ray photoelectron spectroscopy (XPS). Surface activation and brush layer uniformity were evaluated via characterization of surface wettability and AFM analysis. Swelling of the polymer brush layer, in response to changes in salinity and pH, was assessed by determining the rupture length distributions of the tethered polymer chains via single molecule force measurements. Performance of the nano-structured PA RO and PSf UF membranes, with respect to water permeability, salt rejection, fouling resistance and ease of cleaning, at alternating salinity levels, was then quantified for different sections of the large sheet membranes. The results of the current study demonstrate that APPIGP approach can be scaled-up to produce high performance RO and UF membranes with responsive brush layers that decrease membrane fouling propensity and improve cleaning effectiveness.

Keywords: Surface nano-structuring, Atmospheric pressure plasma, Graft polymerization, Responsive membrane

[O7.14]

Smart nanogel-containing membranes in microchip for temperature- and ethanol-responsive permeability regulation

W. Wang*, X.Y. Zou, Y.M. Sun, R. Xie, X.J. Ju, Z. Liu, L.Y. Chu
Sichuan University, China

Recently, integration of membranes in microchips has shown great potential for biomedical fields such as analysis, separation, microreaction and cell-based study, due to their portability and lower consumption of sample and energy. In particular, microchips containing smart membranes that can change their permeability in response to external chemical/physical stimuli are important and necessary, as they can be used as sensors, separators and controlled release systems. Here we report on novel types of smart in-chip membranes containing stimuli-responsive nanogels as nanovalves for self-regulation of permeability. Such smart in-chip membranes can be integrated into microchips by assembly of a pre-fabricated nanogel-containing membrane into microchannels, or *in situ* fabrication of a nanogel-containing membrane in the microchannel. To demonstrate the first strategy for fabricating smart in-chip membranes, a polyethersulfone membrane, prepared by blending poly(*N*-isopropylacrylamide) (PNIPAM) nanogels into the membrane-forming solution via vapor-induced phase separation process, is sandwiched between two polydimethylsiloxane modules of a microchip. To demonstrate the second strategy, a chitosan membrane containing PNIPAM nanogels, is *in situ* fabricated in microchannels, based on crosslinking reaction at the interface between two parallel laminar flows. The PNIPAM nanogels, that allow temperature-responsive and ethanol-responsive swelling/shrinking volume transitions, serve as smart nanovalves for controlling the diffusional permeability of solutes across the membrane. Based on this, both membranes can show excellent temperature- and ethanol-dependent permeability, rapid responsive rate, and good repeatability and stability. These studies provide promising strategies for creation of versatile nanogel-containing smart membranes within microchips via simply changing the functional nanogels for developing micro-scale detectors, sensors, separators and controlled release systems.

Keywords: responsive membranes, nanogel, microchip, permeability regulation

[P2.154]

Ion-responsive smart gating membranes

Z. Liu*, R. Xie, X.J. Ju, W. Wang, L.Y. Chu

Sichuan University, China

Metal ions play important roles in life activities. For examples, alkali metal ion K^+ is the most abundant intracellular metal ion and plays an important role in biological systems. K^+ not only involves in the maintenance of extracellular osmolarity with sodium ion (Na^+) but also regulates the concentration of other ions such as calcium ion (Ca^{2+}) and chloride ion (Cl^-) in the living cell. While heavy metal ion Pb^{2+} can accumulate in the human body through water intake or food chains. The ingestion of lead can cause damage to the central nervous system and dysfunction to the kidneys and immune system of human beings, particularly to children with harmful effects on their intellectual development. Thus, the research of ion-responsive membranes, which are potential for emerging applications such as controlled release of drugs, and detection and removal of toxic ions, is of both scientific and technological interest. Here, we report two kinds of smart membranes with positively K^+-responsive gating and negatively Pb^{2+}-responsive gating properties. The positively responsive gating allows increased membrane permeability when the stimulus appears or increases, while the negatively responsive gating shows reversed property. The proposed positively K^+-responsive membrane is designed with functional gates composed of poly(*N*-isopropylacrylamide) chains and 15-crown-5 units. Due to the cooperative interaction of host-guest complexation, the positively K^+-responsive gating action of the membrane is rapid, reversible and reproducible, resulting in the potential applications of artificial internal organs, controlled release, sensors, early indicators of diseases related with abnormal K^+ concentration in vitro and/or in vivo. The negatively Pb^{2+}-responsive gating membranes are fabricated with poly(*N*-isopropylacrylamide-*co*-acryloylamidobenzo-18-crown-6) copolymers as gates with a large amount of 18-crown-6 units by a two-step method, and are applied for detection and removal of trace Pb^{2+} ions based on cooperative interaction of molecular recognition and polymer phase transition.

Keywords: stimuli-responsive materials, host-guest recognition, smart membranes, gating membranes

[O7.16]

Protein adsorption and desorption behavior of pH-responsive membrane based on ethylene vinyl alcohol copolymer

H. Ye[1,2], Y. Zhang*[1,2], L. Huang[1], Z. Xu[1], L. Zhao[1,2], Q. Xin[2,1], H. Li[1]

[1]Tianjin Polytechnic University, China, [2]State Key Lab of Separation Membrane & Membrane Process, China

The protein adsorption and desorption behavior was investigated for pH-responsive ethylene vinyl alcohol copolymer (EVAL) membrane with the interconnected porous structure. The poly(dimethylaminoethyl methacrylate) (poly(DMAEMA)) chain was used to regulate the protein adsorption properties of the membrane. The maximum static protein adsorption capacity was obtained at pH 6.4. The dynamic adsorption capacity of membrane $EVAL_{10}$ at 10% and 50% breakthrough were 45 and 99 mg BSA/g membrane, respectively. The BSA was quickly desorbed from the membrane and 94% recovery of BSA was observed at pH 9.0. The transition of electrostatic behavior and conformation change of the poly(DMAEMA) chain would contribute to the pH-responsive protein adsorption and desorption of the membrane. The dynamic adsorption capacity of the membrane did not change significantly after three sequential cycles. Such pH-responsive EVAL membrane shows good prospects for protein purification.

Keywords: responsive membrane, EVAL, membrane adsorber, adsorption

[O7.17]

Modification of polycarbonate membranes with EDC/NHS coupling: Impact on rejection of polystyrene particles

A. Delavari[1], D. Breite[2], R.E. Baltus*[1], A. Schulze[2]
[1]Clarkson University, USA, [2]Leibniz Institute of Surface Modification, Germany

In this work, the impact of physicochemical interactions between solid particles and porous membranes has been examined from both experimental and theoretical perspectives.

Commercially available polycarbonate track etched membranes and polystyrene particles both carry a strong negative surface charge. To create an experimental system with different particle-pore wall interactions, membranes were modified using an EDC/NHS coupling reaction with tetraethylpentamine, creating a set of membranes with reduced surface charges and no measurable change in pore size. Streaming potential measurements were used to determine pore surface characteristics. The rejection of negatively charged red dyed spherical polystyrene particles was measured using a 10 ml dead-end filtration cell with both modified and non-modified membranes. The impact of flow rate, rotational stir speed and feed concentration on measured rejections was examined for both types of membranes.

When compared to particle rejections observed with non-modified membranes with the same pore size, larger rejections (up to 36% increase) were observed with the modified membranes because electrostatic repulsion between particle and membrane is reduced with the pore surface modification. Examination of the impact of flow rate and stir speed on rejections illustrate the complexity of the particle-pore wall interactions for these systems.

To analyze the forces governing particle transport and rejection, several computational models were developed and coupled. These included macroscale models of the filtration cell (using the k-epsilon turbulent flow model) and the membrane (using the Brinkman equation) and a microscale model of a single pore. Hydrodynamic and electrostatic forces on the particle surface at the pore entrance were calculated. Results were compared with experimentally measured rejection values; observations were found to be consistent with theoretical particle force calculations.

The results from this study provide insight into the impact of electrostatic particle-pore wall interactions on rejection of particles in porous membranes.

Keywords: Surface Modification, rejection model, microfiltration, Porous membranes

[O7.18]

Tailor-made star-shaped polymers for surface functionalization of porous membranes toward switchable permeability and specific adsorber properties

J. Brückerhoff*, M. Ulbricht
University of Duisburg-Essen, Germany

An innovative approach for functionalization of porous membranes to add stimuli-responsive and metal ion adsorptive properties is established in this work. Tailor-made star-shaped polymers are synthesized with β-cyclodextrin (βCD) as well-defined core using controlled atom transfer radical polymerization (ATRP) from pre-functionalized βCD as macro-initiator.[1] This enables obtaining macromolecules with 7 or 21 "arms" of uniform lengths, leading to globular shape with hydrodynamic radii from few to several 10 nanometers and high density of functional groups, all adjustable by ATRP conditions. The macromolecular arms also contain a fraction of reactive groups to couple the polymer to the membrane surface via "click" chemistry, based on 1,3-cycloaddition between star polymer and membrane surface, respectively. PET track-etched membranes are used as model system for evaluation because their loading with star-shaped polymers can easily be analyzed due to the isocylindrical pore shape; the degree and effects of pore functionalization can also be quantified using flux measurements.[2] The first generation of star-shaped polymers contains poly(dimethyl-aminoethyl methacrylate) (PDMAEMA) arms, co-polymerized with "click"-able propargyl-acrylate. Besides chemical characterization, colloidal properties are analyzed by dynamic light scattering and ultrafiltration using a range of commercial membranes with different molecular size cut-off. Pre-functionalized PET track-etched membranes with "click"-able azide groups, functionalized with star-shaped polymers show stimuli-responsive water permeability and adsorber properties for heavy metal ions. Depending on degree of protonation and resulting conformation of the macromolecular arms, these properties can be switched by stimuli such as pH value or temperature (Figure 1). After detailed analysis of the properties of the PET model membranes functionalized with star-shaped polymers, this approach is currently extended to functionalization of anisotropic cellulose ultrafiltration membranes leading to materials with combined size and adsorber selectivity. In summary, we present a novel versatile, modular approach to functionalize porous membranes to tailor a range of different interesting and relevant properties.

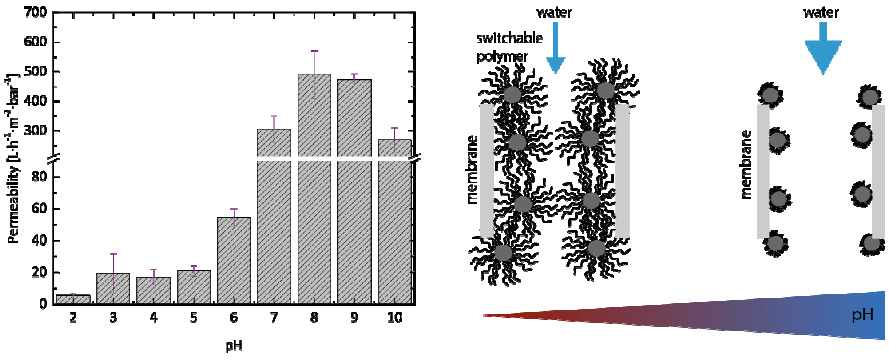


Figure 1: Star-PDMAEMA functionalized PET track-etched membrane with pH-dependent water permeability.

References

[1] X. Pang, L. Zhao, M. Akinc, J. K. Kim, Z. Lin, *Macromolecules* **2011**, 44, 3746–3752.

[2] Q. Yang, N. Adrus, F. Tomicki, M. Ulbricht, *J. Mater. Chem.* **2011**, 21, 2783–2811.

Keywords: click chemistry, star polymers, stimuli-responsive, membrane adsorber

[O7.19]

Mussel-inspired superoleophobic surface modification for robust membrane distillation performance

N.G.P. Chew*[1,2], S. Zhao[2], C. Malde[3], R. Wang[1,2]

[1]Nanyang Technological University, Singapore, [2]Singapore Membrane Technology Centre, Singapore, [3]Johnson Matthey Technology Centre, UK

With its many advantages, direct-contact membrane distillation (DCMD) appears to hold potential for the recovery of high quality water from produced water. However, membrane fouling and pore wetting are challenging issues of long-term DCMD operations due to the presence of oils and surfactants in these waters. Hence, it is paramount to develop robust membranes with anti-fouling and anti-wetting properties for effective produced water treatment.

In this study, we fabricated a composite hollow fiber membrane by single-step co-deposition of polydopamine (PDA)/polyethylenimine (PEI) onto the outer surface of a commercial hydrophobic polyvinylidene fluoride (PVDF) substrate. The successful co-deposition was verified using different characterization techniques. The composite membrane exhibited Janus wettability (Janus membranes are membranes with opposing properties at an interface) with its modified outer surface being underwater superoleophobic for preventing organics adhesion while insuring that unmodified pores beneath the surface remained hydrophobic for vapor transport.

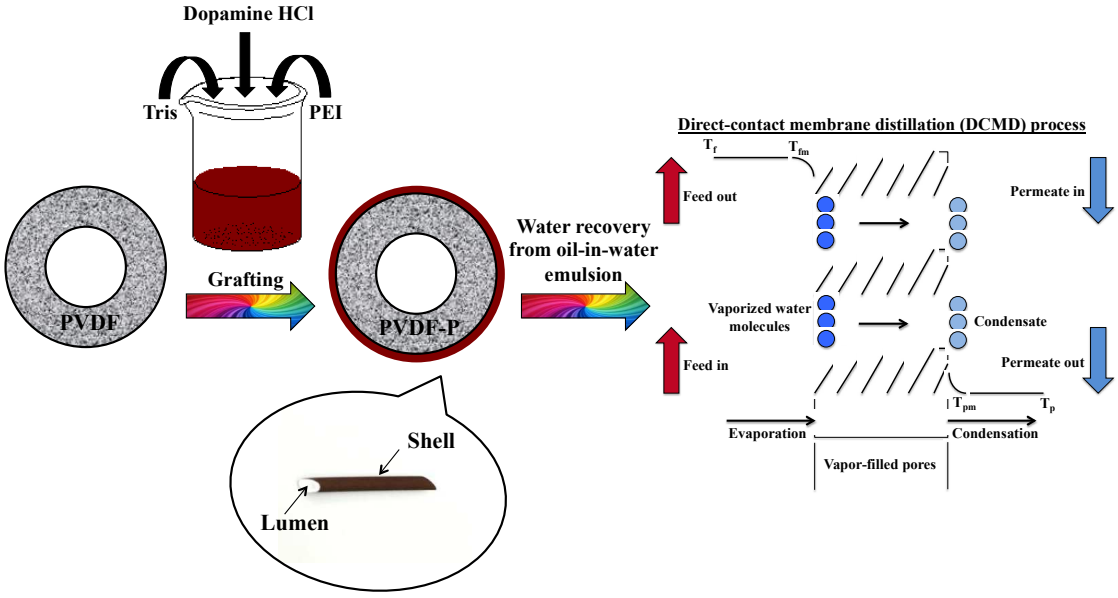


Fig. 1. Schematics of co-deposition of PDA/PEI on the outer surface of a PVDF membrane and its application in water recovery from oil-in-water emulsions via DCMD.

The anti-fouling and anti-wetting properties of the modified membrane were investigated via DCMD experiments by feeding a series of low surface tension solutions. In comparison to the pristine PVDF membrane, the modified membrane exhibited a promising wetting resistant property against different surfactant types and an excellent fouling resistant property against nonionic and cationic surfactants. Moreover, the modified membrane presented a promising long-term performance when feeding a cationic surfactant-stabilized petroleum-in-water emulsion mimicking produced water, during which a stable flux and excellent permeate quality were maintained throughout 7 days of operation. The efficacious combined effects of a hydration layer and protonated amine-functional groups on the PDA/PEI grafted layer could prevent membrane fouling and pore wetting. The results suggest that the mussel-inspired composite PVDF membrane could potentially be used for long-term water recovery from produced water via DCMD.

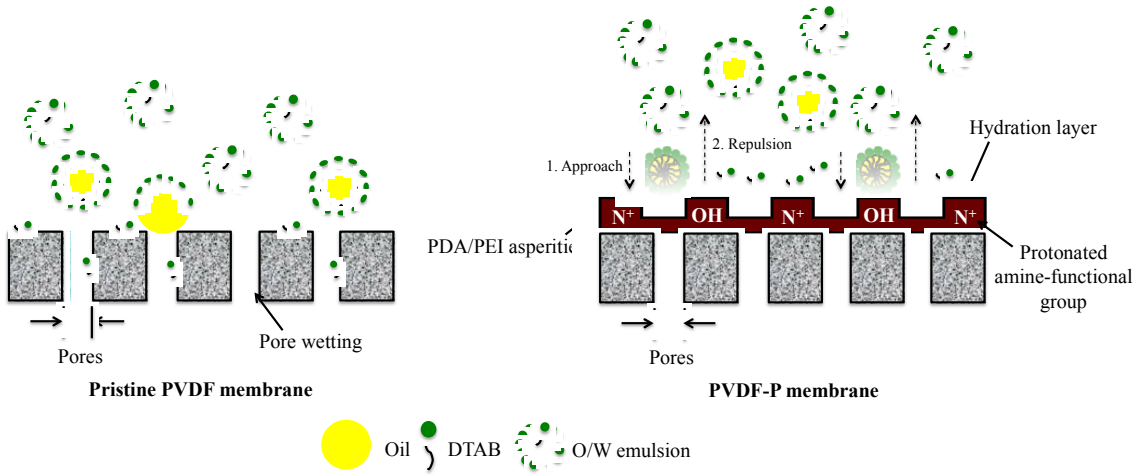


Fig. 2. Schematic of interaction of DTAB-stabilized petroleum-in-water emulsion with the pristine PVDF and PVDF-P membranes.

Keywords: Polydopamine, Polyethylenimine, Membrane distillation, Surface modification

[O7.20]

Surface engineering of polymeric membranes: What is the impact of pre-treatment on sequential vapor phase nanoparticle deposition?

A. DeStefano*, J. Yin, T. Kraus, B. Parkinson, D. Li
University of Wyoming, USA

Surface properties of commercial polyvinylidene fluoride (PVDF) ultrafiltration (UF) membranes were modified using a dopamine (DA) self-polymerization pretreatment followed by thermal atomic layer deposition (ALD) at 100□C of titanium dioxide (TiO_2). Resulting membranes were characterized using water contact angle, SEM/EDS, and AFM. We aim to study how the combination of relatively short DA dip coating time (15 minutes) and low number of ALD cycles (<100) changes surface properties of hydrophobic polymer membranes, including hydrophilicity and roughness, and corresponding water and bovine serum albumin (BSA) flux.

Our results showed that ALD-TiO_2 onto PDA treated membranes had finite penetration into the membrane cross-section. In addition, a nonlinear relationship between the number of ALD cycles performed and the water contact angle and surface roughness was observed. Both initially decreased with PDA treatment and increasing ALD cycles, but had a maximum with 60 ALD cycles, further confirming that low surface energy of hydrophobic polymer surfaces renders dopamine coating mechanism challenging to elucidate.

To corroborate surface property change with filtration performance, neat and surface-modified membranes were evaluated using dead end filtration of deionized water and BSA solution. With dopamine treatment before ALD-TiO_2, water flux varied nonlinearly, while contaminant rejection increased with the number of ALD cycles. Filtration trends were generally consistent with surface roughness and water contact angle. Comparison of direct TiO_2 via ALD onto PVDF UF membranes, dopamine and/or ethanol pretreatment before ALD-TiO_2 showed the highest water flux and BSA rejection without pretreatment for the conditions we investigated.

Keywords: atomic layer deposition, ultrafiltration, polydopamine, titanium dioxide

[O7.21]

A highly selective and antimicrobial membrane coating for thin-film composite membrane modification: Mechanism and implications

Z. Yang*[1], Y.C. Wu[2], J.Q. wang[1], B. Cao[2], C.Y. Tang[1]

[1]The University of Hong Kong, Hong Kong, [2]Nanyang Technological University, Singapore

In this study, a highly selective and antimicrobial surface coating was designed for thin-film composite (TFC) membrane modification. The polyamide layer was first coated with polydopamine (PDA), whose catechol groups could *in situ* immobilize silver ions to form uniformly distributed silver nanoparticles in the PDA coating layer. The resulting PDA/Ag coated membranes showed high silver loading of 13.3 ± 0.3 μg/cm^2 with surface coverage ratio of 18.5% by the nanoparticles. Membrane antimicrobial tests (diffusion inhibition zone tests and colony formation unit tests) showed good antimicrobial effects of the PDA/Ag TFC membranes on mode bacterial *Bacillus subtills* and *Escherichia coli*. We further report self-healing mechanism of the PDA/Ag coating layer based on the significantly enhanced salt rejection with slightly reduced water permeability compared to the control PDA coated membrane, which was attributed to the preferential formation of silver nanoparticles in the PDA layer. The self-healing mechanism can be applied to synthesize antimicrobial TFC membranes with improved water/salt selectivity without sacrificing the membrane water permeability, which provides a new avenue for membrane surface coating.

Keywords: Thin-film composite membranes, Polydopamine, Antimicrobial membranes, Selectivity

[O7.22]

Thermodynamic understanding of membrane-biofoulant interfacial interactions: Implication of membrane electron-donocity

D.W. Jun, B. McVerry, N. He, X. Huang, J. Yang, E. Hoek, R. Kaner, D. Chen*
University of California, USA

Since the majority of biofouling occurs on the surface of polymeric membranes, interfacial interactions between a membrane surface and a biofoulant play a pivotal role in biofouling phenomena. Here we investigate the thermodynamic mechanism of biofouling based on the XDLVO theory. The results of the thermodynamic analysis will be discussed along with experimental results of several biofouling tests (microbial adhesion test, alginate fouling test, and fouling test in a lab-scale membrane bioreactor) using three different polymeric UF membranes (PVDF, PES, and PAN). Furthermore, we attempt to impart a commercial PES UF membrane with hydrophilic and anti-biofouling properties by grafting hydrophilic polymers onto the surface, and examined the impact of different interfacial properties of the membrane surface on biofouling.

According to our XDLVO analysis, the high electron-acceptor properties of water emphasizes the importance of electron-donicity of a membrane and a biofoulant in their interfacial interactions through water, which induces acid-base phenomena that are a major component in the interfacial interactions. Experimental results of microbial adhesion tests and biofouling tests qualitatively correlate well with tendencies of electron-donicities of the test membranes, providing evidence for an electron-donicity of a membrane to be a reasonable indicator of anti-biofouling properties.

Photoactive perfluorophenyl azides (PFPAs) were utilized to covalently bind several hydrophilic polymer grafts to the PES membranes. The analyzed physicochemical properties of the modified membranes are compared to the experimental results of biofouling tests with alginate solution. The modified membranes with higher electron-donicity exhibited outstanding fouling-resistance against the alginate foulant.

Keywords: Interfacial interaction, Anti-biofouling, Surface grafting, XDLVO

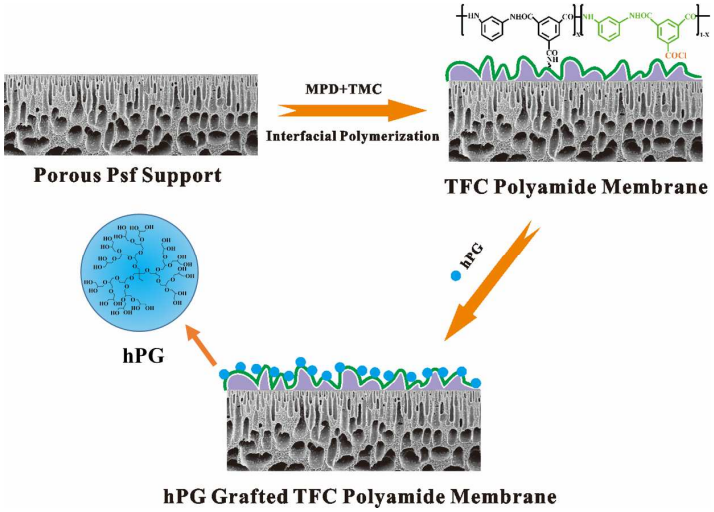
[O7.23]

Surface engineering of thin film composite polyamide membranes with nanoparticles-like hyperbranched polyglycerol for improving antifouling properties

Z. Liu*[1,2], B. Mi[2], Y. Hu[1], X. An[1], C. Dong[1]

[1]Chinese Academy of Sciences, China, [2]University of California, USA

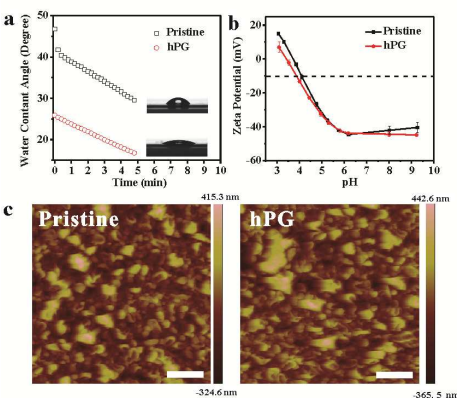
Introduction: Thin-film composite (TFC) polyamide membranes as state-of-the-art membranes have been widely used for nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO) applications. However, owing to the intrinsically physiochemical properties of polyamide layer, TFC membranes are still highly susceptible to irreversible membrane fouling, which significantly compromises their water flux, produced water quality and separation efficiency. Nanoparticle-like hyperbranched polyglycerol (HPG) is considered as a superior building block for surface antifouling modification due to its well-preserved end hydrophilic hydroxyl groups and unique 3D globular-shaped architecture. Therefore, in this study, HPG was synthesized and grafted onto the polyamide surface to improve resistance of TFC polyamide membrane toward foulants, thereby enabling their long-term good performance in real operation.



Scheme 1. Incorporation of HPG onto polyamide surface of TFC membrane through layer-by-layer interfacial polymerization

Methods: In this study, HPG was first synthesized via anionic ring opening polymerization of glycidol, and then was grafted to the polyamide surface during the fabrication process of TFC membrane via layer-by-layer interfacial polymerization, as shown in Figure 1. The effects of incorporation of HPG on the hydrophilicity, surface charge and roughness of polyamide layer as well as the water flux, salt rejection and antifouling property of TFC membrane were systematically investigated.

Results:



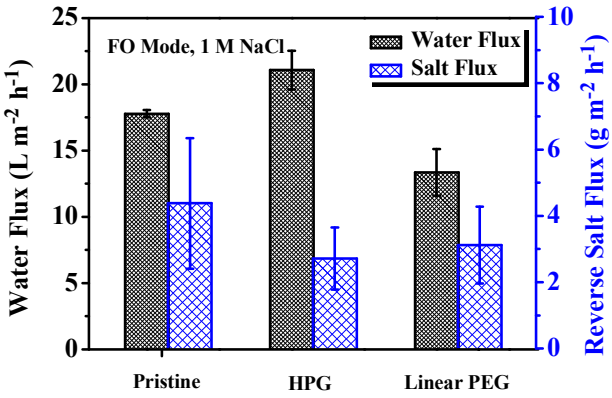


Figure 1. The hydrophilicity, surface charge, and roughness of polyamide layer (left) as well as the water flux and salt rejection (right) of pristine and HPG grafted TFC membranes. Scale bars: 500 nm.

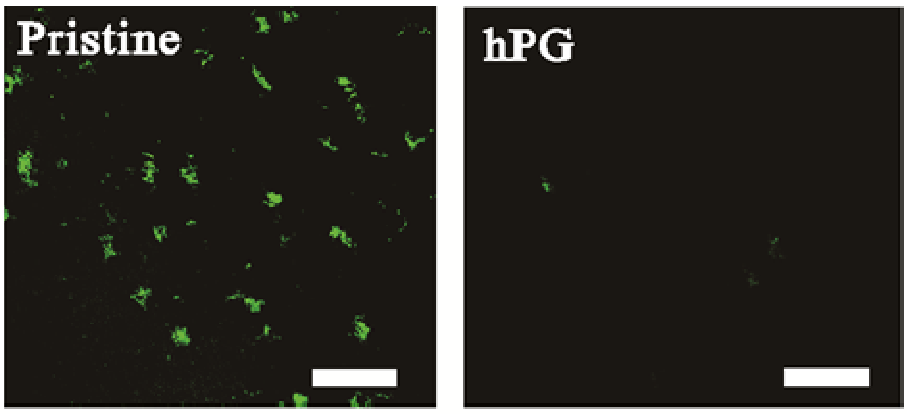


Figure 2. Representative laser confocal microscopy images of adsorbed FITC labelled BSA on polyamide layer of pristine and HPG grafted TFC membranes. Scale bars: 20 μm.

Discussion: Our results demonstrated that the incorporation of HPG increased the hydrophilicity of polyamide layer significantly due to abundant end hydrophilic hydroxyl groups of HPG, and showed negligible effects on the surface charge and roughness of active layer, as shown in Figure 1. Fouling resistance of HPG functionalized membrane against BSA as well as their permeability and rejection were improved in comparison to pristine membrane, implying the promising prospect of HPG as next-generation material for improving the antifouling property of TFC membranes.

Keywords: Thin film composite polyamide membranes, Hyperbranched polyglycerol, Antifouling

[O7.24]

Organic solvent nanofiltration membranes developed by mussel-inspired co-deposition strategy

L. Shao*, Y.C. Xu

Harbin Institute of Technology, USA

Introduction: Most of the reported nanocomposite solvent nanofiltration (OSN) membranes were fabricated by interfacial polymerization or direct coating method. Interfacial polymerization suffers sophisticated multistep fabricating steps, while direct coating usually yields separation layer with thickness up to tens of micrometers. In this study, we demonstrate a highly-efficient mussel-inspired co-deposition strategy to fabricate nanocomposite OSN membranes, as shown in Figure 1.

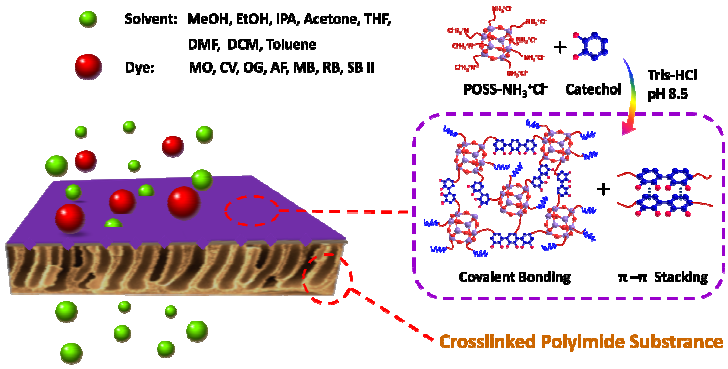


Figure 1.Schematic illustration of the fabrication of novel nanocomposite OSN membranes.

Methods: The cross-linked polyimide P84 UF substrates were immersed in a pH 8.5 buffer solution containing catechol (1 mg mL^{-1}) and POSS-$NH_3^+Cl^-$ with various mass ratios and shaked at 30 ^oC for a certain time.

Results: ATR-FTIR spectra (Figure 2(A)) show the modified membrane exhibits a new peak related to POSS after co-deposition. XPS spectra (Figure 2(B)) disclose a highest Si atom concentration at a POSS-$NH_3^+Cl^-$/catechol mass ratio of 5:1. Membrane morphologies (Figure 2(C) and 2(D)) of modified membranes reveal the nanopores at pristine support vanished and the surface became rough after co-deposition. The optimized nanocomposite membrane exhibited an ethanol (EtOH) permeance of 1.26 L m−2 h−1 bar−1 with a rejection of 99% to Rose Bengal (RB). The novel membrane also exhibited remarkable separation performance for dyes removal from a wide range of solvents including challenging polar aprotic and strongly swelling solvents. Particularly, the nanocomposite membrane demonstrated stable performances during a two-day long term test in DMF for RB concentration. In addition to providing a highly-efficient way to high-performance OSN membrane, this work may stimulate the bio-inspired design of advanced nanocomposite membranes for environmental applications.

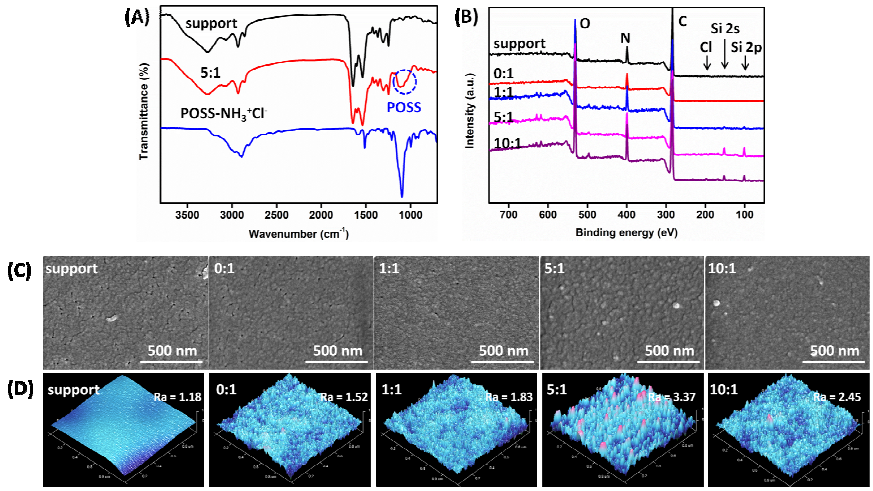


Figure 2. (A) ATR-FTIR spectra of support, typical co-deposited membrane and POSS-$NH_3^+Cl^-$; (B) XPS spectra, (C) SEM images and (D) AFM images of membranes modified with various POSS-$NH_3^+Cl^-$/catechol mass ratios.

Figure 3(A) shows the optimized nanocomposite membrane exhibited an ethanol (EtOH) permeance of 1.26 L $m^{-2}h^{-1}bar^{-1}$ with a Rose Bengal rejection of 99%.

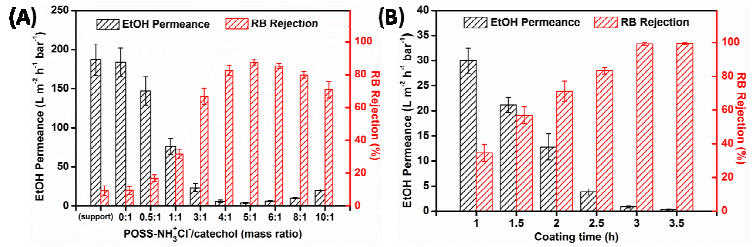


Figure 2. Separation performances of co-deposited membranes in terms of (A) POSS-$NH_3^+Cl^-$ /catechol mass ratio (coating time 2.5 h) and (B) coating time (POSS-$NH_3^+Cl^-$/catechol mass ratio of 5:1).

Discussion: A one-step mussel-inspired co-deposition strategy has been discovered to fabricate novel nanocomposite OSN membranes. The resultant nanocomposite membrane shows high performances in OSN application, which could be due to the rigid inorganic POSS cages could provide preferential flow path for small solvent molecular.

Keywords: mussel-inspired, modification, nanofiltration, highly efficient

[O7.24]

HELIX - Flux enhancement technology in tubular waste water treatment membranes

J. Potreck*
Pentair X-Flow, The Netherlands

Tubular ultrafiltration membranes are used in the separations of high solid streams, e.g. sludge from bioreactors. Due to the fouling behavior of the sludge and the application of crossflow, these membranes suffer from concentration polarization and fouling.

To overcome fouling and to increase the mass transfer, the smooth surface of the polymeric membrane has been structured with a ridge, helically wound along the wall. This macroscopic surface modification has led to a drastic improvement of performance. The increased level of turbulence at the membrane wall generates a substantially thinner boundary layer which has improved the fluxes by a factor of two in certain MBR applications. Since the ridge is from the active membrane material itself, the area participating in filtration is not restricted and does not attract deposition of fouling.

The technology has been tested in pilot as well as full scale installations around the world with consistently higher performance to unmodified membranes. Results of the pilot as well as full scale installations will be shown and significantly improved energy balances for the waste water treatment plants are investigated resulting in comparable or even better performance than conventional or other membrane treatment processes.

This technology has been launched in 2015 as Compact HELIX membrane. The HELIX technology has been patented by Pentair X-Flow.

Keywords: Flux enhancement, Tubular membranes, MBR, HELIX

[O7.25]

Novel high-performance nanofiltration membranes with full pH-stability

N. Daems*[1], P.P. Pescarmona[2,1], I.F.J. Vankelecom[1]
[1]K.U. Leuven, Belgium, [2]R.U. Groningen, The Netherlands

Currently, nanofiltration membranes attract a lot of interest in the field of separation, as it offers economical and ecological advantages in comparison with conventional separation technologies, including easy upscaling, no waste creation and low energy consumption.[1] Unfortunately, most commercially available NF membranes have thus far shown limited stability at extreme pH conditions or suffer from low permeability or a too high molecular weight cut-off. Thus, following current strong demands from paper, food and mining industries for nanofiltration membranes with a chemical stability over the full pH-range, a novel membrane type is presented consisting of polyvinylidene fluoride (PVDF) grafted with polystyrene sulfonic acid (PVDF-g-PSSA).

In this work, a strategy was developed to further extend the use of PVDF to the NF range by grafting the large pores of PVDF membranes with polystyrene to create a denser membrane. Subsequently, sulfonic acid groups were introduced into this polystyrene to further enhance the salt retention through Donnan exclusion. The performance of these PVDF-g-PSSA membranes was investigated by means of high-throughput filtration experiments using aqueous solutions of dyes of different size as well as salt solutions before and long term exposure to extreme pH-condtions.

After grafting and sulfonation, the membrane performance clearly increased (**Table 1**) as is evidenced by an increased permeance, which is a consequence of the more hydrophilic membrane nature, and an enhanced salt and dye retention, which is both a consequence of the presence of the extra polystyrene layer and the presence of the ionic groups.

Table 1. Retention for the different solutes and water permeance for the parent PVDF and the PVDF-g-PSSA membrane.

Solute	Permeance [L h^{-1} m^{-2} bar^{-1}]	Retention [%]		
		Rose Bengal	Rhodamine B	NaCl
PVDF	3.0±0.5	99.9±1.0	61.0±0.6	17.9±8.2
PVDF-g-PSSA[b)]	4.4±0.5	99.9±0.4	96.0±0.8	39.7±0.8

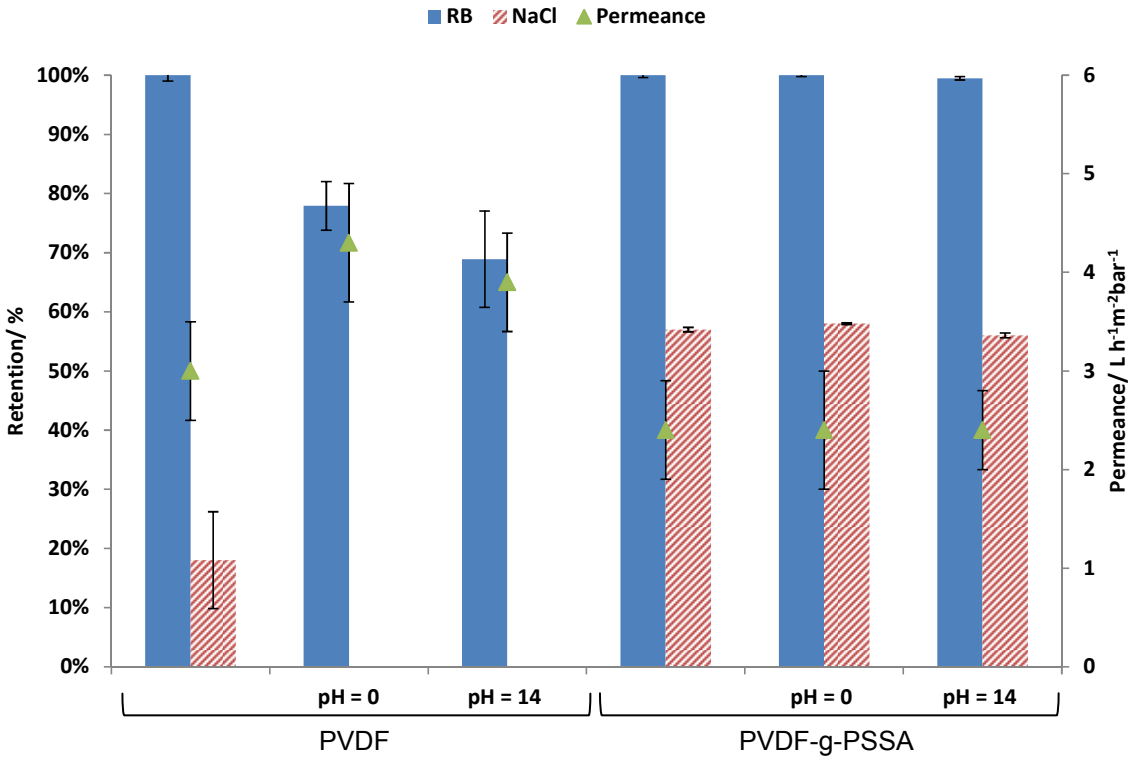


Figure 1. Influence of treatment at extreme pH on the permeance and on the salt and dye retention for PVDF and PVDF-g-PSSA-3.

From **Figure 1**, it can be observed that the performance of the PVDF-g-PSSA membrane remains constant after exposure to extreme pH for 1 week.

A novel type of membrane was thus prepared, combining an excellent separation performance in the NF-range with complete stability over the full (0-14) pH-range.

[1] M. Mulder, *Basic Principles of Membrane Technology*; second ed.; Kluwer Academic Publishers: Dordrecht, 1996.

Keywords: Polyvinylidene fluoride, sulfonated, nanofiltration, pH-resistant

[O7.26]

Incorporation of oleic acid-modified Ag@ZnO core-shell nanoparticles into thin film composite membranes for enhanced antibacterial properties

Y.B. Chen*, X.J. Huang, S.Y. Wei, Y.F. Zhang

Tianjin Polytechnic University, China

Polyamide (PA) membranes with good hydrophilic, chemical stability and separation performance have been utilized as nanofiltration membranes, but poor antifouling and antibacterial properties of PA membrane hinder its further development. In this study, Ag@ZnO/PA thin film nanocomposite (TFN) membranes were prepared by dispersing oleic acid (OA)-modified Ag@ZnO core-shell nanoparticles (playing a role as antibacterial agent) in trimesoyl chloride (TMC)-hexane solution via interfacial polymerization. The Ag@ZnO nanoparticle crystalline structure in the TFN membranes was confirmed by X-ray diffraction and transmission electron microscopy. Surface morphology, roughness, chemical properties, hydrophilicity and charge of synthesized membranes were characterized by scanning electron microscopy, atomic force microscopy, Fourier transform infrared spectroscopy, contact angle and zeta potential analysis. The results showed that incorporating OA-modified Ag@ZnO into PA layer improved chemical and physical properties of TFN membranes. The effect of addition of OA-modified Ag@ZnO nanoparticles on pure water permeability and Na_2SO_4 or NaCl rejection were investigated. The maximum Na_2SO_4 and NaCl rejections for OA-modified Ag@ZnO/PA membrane were obtained about 98.6% and 59.5%, while the rejections of PA thin film composite (TFC) membrane were only 94.5% and 49.5%, respectively. Compared with TFC membrane, OA-modified Ag@ZnO/PA membrane showed lower flux decline rate during BSA solution filtration and higher flux recovery rate after water flushing. Besides, excellent antibacterial against E. coli and B. subtilis and long term Ag^+ release rate of OA-modified Ag@ZnO/PA membrane is expected to become a potential antifouling and antibacterial nanofiltration membrane.

Keywords: thin film nanocomposite, nanofiltration, antibacterial, antifouling

[O7.27]

Graphene oxide top layer for water treatment and separation mechanisms for salts, dyes, and protein solutions

F. Baskoro, S.J. Lue*

Chang Gung University, Taiwan

In this work, graphene oxide (GO) is used as ultrathin separation layer on composites to prepare water selective membranes for purification processes. The synthesized ultrathin GO separation layer is distributed on the top surface of a micro-porous polyvinylidene fluoride-polyacrylic acid (PVDF-PAA) intermediate layer, formed on a non-woven support to improve the mechanical properties of the three-layer composite membranes. The resulting membranes are tested on a nanofiltration (NF) system to examine the water permeability and solute rejection efficiency for salts, dyes, and protein solutions. The rejection performance was 99 % for Na_2SO_4, 80 % for rhodamine-B and 86 % for methyl orange. High rejections of bovine serum albumin (BSA) are obtained on both three-layer composite and the GO-free two-layer membranes. The water permeation performance through the GO composite membrane follows modified Hagen-Poiseuille's law. The separation efficiencies are mainly due to contribution of Donnan exclusion mechanism for salt solutions and sieving mechanism for organic dyes. The long-term NF operation shows the anti-fouling property of GO composite membranes. The high performance of the GO composite membrane exhibits potential for separation and purification on aqueous solutions of salts, dyes, and proteins.

Keywords: Graphene oxide, Separation mechanism, Thin film composite, Water purification

[O7.28]

Solvents in membrane synthesis and their effect on NF/RO performance: From conventional organic solvents to ionic liquids

H. Mariën*, L. Bellings, S. Hermans, I.F.J. Vankelecom
KU Leuven, Belgium

Organic solvents are a key element in the preparation of nanofiltration (NF) and reverse osmosis (RO) membranes and have a major impact on membrane morphology. In this work, the beneficial effect of the use of ionic liquids (ILs) as organic reaction phase in interfacial polymerization (IFP) as well as the application of post-synthesis solvent treatments on integrally skinned asymmetric (ISA) and thin-film composite (TFC) membranes is shown.

First, commonly used **hexane or isopar in IFP was replaced by an IL** to improve the polyamide top layer morphology. The **influence of the physicochemical properties of the IL** ($[C_4mim][Tf_2N]$) **was immense** (Figure 1). They allowed to lower the m-phenylenediamine concentration in the aqueous phase with a factor 20 and to omit the use of common additives. Moreover, the top layer was significantly thinner and smoother, resulting in a higher water permeance and a lower fouling tendency. The IL was recycled for consecutive IFP cycles, realizing a 64% decrease in mass intensity of the top layer formation.

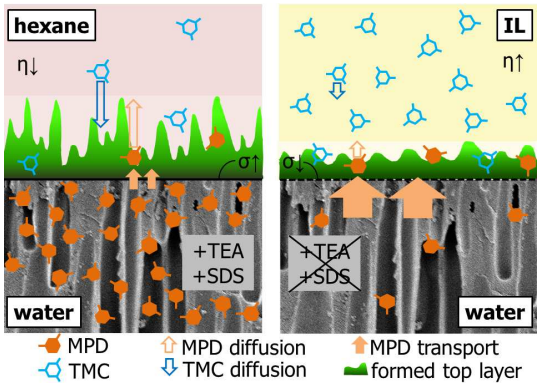


Figure 1: Schematic representation of the effects of the organic solvent properties on top layer formation in the conventional IFP (left) and the IL-based IFP (right).

In the second part, the effect of **post-synthesis solvent treatments** was investigated, both on ISA and TFC membranes.

- It is hypothesized that non-cross-linked **polyamide oligomers diffuse out of the top layer of TFC membranes** during the treatment, increasing the free volume and improving the permeance (Figure 2). In this work, oligomer leaching was **confirmed** via H-NMR and GPC analysis, and its effect was further **enhanced**.

- In the preparation of cross-linked polyimide **ISA membranes**, solvent treatment had the opposite effect, i.e. the permeance decreased, while the retention increased drastically. A strong membrane-solvent affinity is assumed to cause polymer chain flexibility and **rearrangement towards a more dense packing** to improve interchain interactions (e.g. hydrogen bonding, π-interactions and further cross-linking) (Figure 3). Via this treatment, **high-performance NF membranes with significantly higher permeance** compared to commercial ISA membranes were obtained.

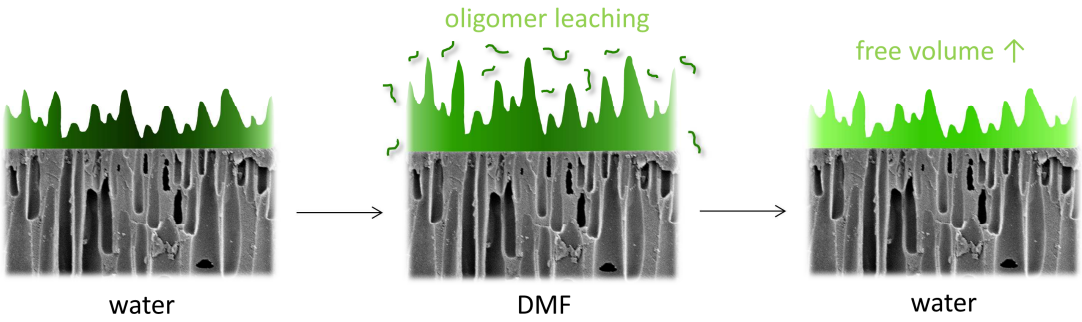


Figure 2: Schematic representation of the effect of a DMF treatment on TFC polyamide/cross-linked polyimide membranes.

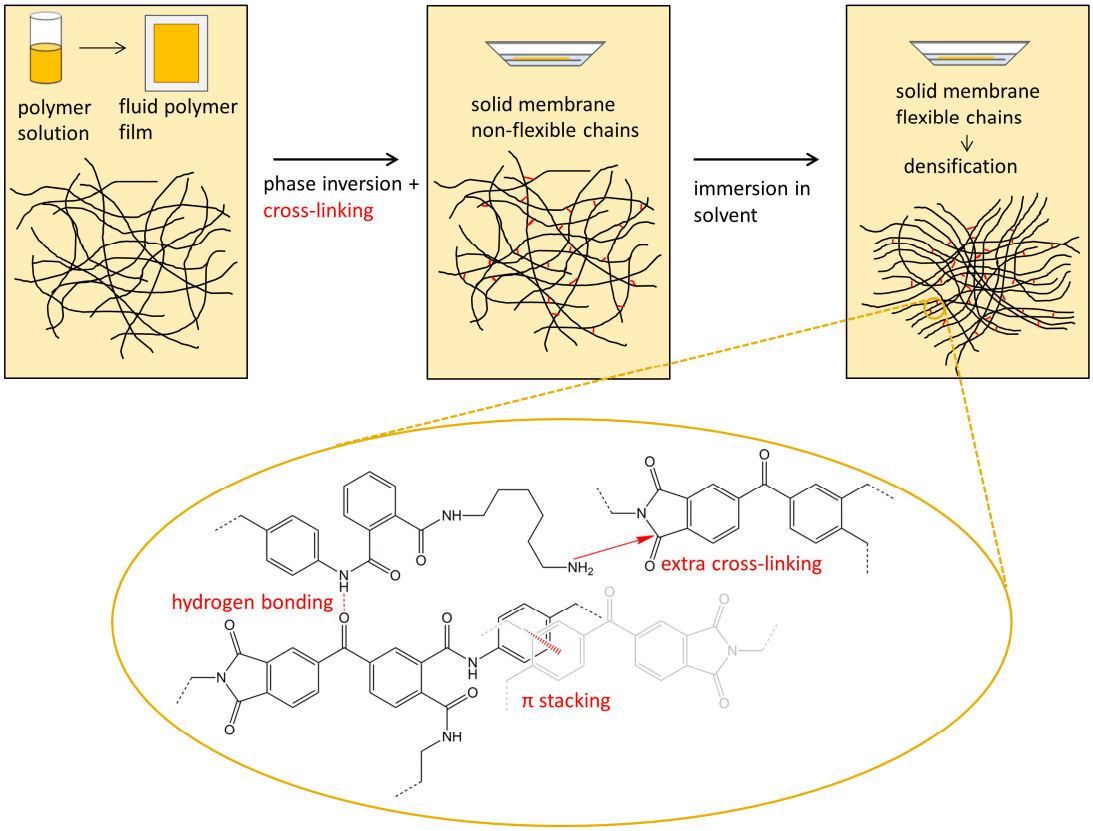


Figure 3: Schematic representation of the effect of a DMF treatment on cross-linked ISA polyimide membranes.

Keywords: interfacial polymerization, ionic liquids, solvent activation

[O7.29]

Preparation of nanofiltration membranes via alternating polyelectrolyte deposition with limited number of layers on PSF/SPES based porous support membranes

O. Tekinalp*, S.A. Altinkaya

Izmir Institute of Technology, Turkey

Nanofiltration membranes are usually prepared in thin film composite structure through polymerization of various monomers or coating of previously synthesized polymer on porous support membranes. Layer by layer deposition of polyelectrolytes on a porous support is a facile and convenient method for the sake of producing nanofiltration membranes. The method offers several advantages such as high selectivity in the passage of water relative to the passage of salt ions due to high water adsorption capacities of the polyelectrolytes and presence of ionic groups, flexibility in adjusting the thickness, charge density and composition of the selective layer by carefully selecting the deposition conditions and polyelectrolyte pairs.

This study intends to manufacture thin film composite nanofiltration membrane via alternating polyelectrolyte deposition with limited number of layers on polysulfone/sulfonated polyethersulfone (PSF/SPES) porous support membrane. Polyethyleneimine (PEI) and alginate were chosen as polyelectrolyte pairs. The support membranes with different pore sizes were prepared via nonsolvent induced phase inversion method by changing compositions of casting solution and coagulation bath as well as thickness of the casting solution. The polyelectrolytes were deposited dynamically in a dead end filtration module at 1 bar. The influences of number of layers, pH and salt concentration in polyelectrolyte solution and molecular weight of PEI on the water fluxes and rejection of the membranes were investigated. The membranes were characterized by SEM, AFM, zeta potential and contact angle analyses. Fouling tendency of produced membranes was determined with BSA solution. We demonstrated that nanofiltration membrane (83 % PEG1000 rejection) with a high flux (14 L/m^2.h.bar) can be manufactured by even depositing a single layer of PEI. We have found that in order to deposit as few as 3 layers and still obtain membranes in nanofiltration range, the molecular weight cutoff value of the support membrane should be less than 10 kDa.

Keywords: Layer-by-layer assembly, Nanofiltration, Polyethyleneimine/Alginate/Polysulfone/Sulfonated Polyethersulfone, Phase inversion

[O7.30]

Constructing zwitterionic surface of nanofiltration membrane for high flux and antifouling performance

Y-F. Mi*[1], Y-S. Guo[1], X-D. Weng[1], F-Y. Zhao[1], Q-F. An[1,2]

[1]ZheJiang University, China, [2]Beijing University of Technology, China

Fouling phenomenon is a serious challenge during the nanofiltration process, which leads to the unacceptable reduction of separation efficiency and obvious increase of maintenance/operation cost. Surface modification suggests an effective strategy to tune the characteristics of membranes, hence suppress the fouling phenomenon. Zwitterions, possess both negative and positive charged units and create strong and more stable hydration layer, have been demonstrated as a promising approach to both alleviate membrane fouling problems and increase membrane water flux. Therefore, this work report a method of surface modification to anchor zwitterion moieties onto the membrane surfaces in situ, which could not only avoid introducing dense modification layer but greatly improve the membrane performance. In this study, surface zwitterionization was conducted by 1, 3-propanesultone ring-opening directly on the nanofiltration membrane prepared by interfacial polymerization of 3, 3'-diaminodipropylamine and 1, 3, 5-benzenetricarboxylic chloride. The membranes were characterized by ATR-FTIR, XPS, SEM, AFM, water contact angle and zeta potential. The zwitterionic structures improve the hydrophilicity of nanofiltration membrane, thus increase the water permeability and antifouling performance. The zwitterionic membrane have a 72 L m^{-2} h^{-1} water flux at the optimize condition, which was about 2.4 times that of the pristine membrane without zwitterionization, and with a 89% rejection of $MgCl_2$. Meanwhile, the zwitterionic membrane will have better antifouling performance to protein and polysaccharose. The flux recovery ratio of bovine serum albumin, sodium alginate and lysozyme were all above 95%. The prepared zwitterionic membrane presents prominent high water flux and fouling-resistance performance, indicating it's promising application potential in organic wastewater treatment.

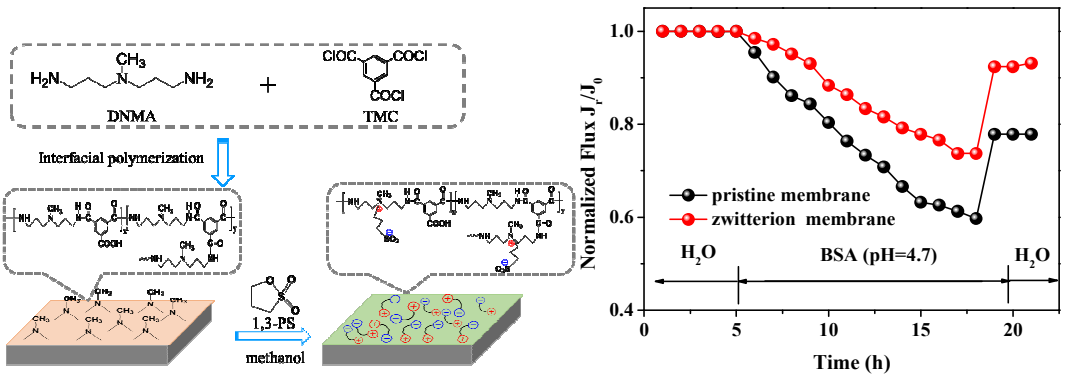


Fig. 1 Schematic illustration of fabrication process of zwitterionic surface membrane (left) and antifouling performance (right).

Keywords: zwitterion, nanofiltration membrane, surface modification, antifouling performance

[O7.31]

Epon resin 1031-based TFC-membranes via nucleophilic and anionic ring opening polymerization

E. Dom[1], J. Van den Bosch[1], S. Rutten[1], J. Vandendriessche[1], T. Koschine[1], A. Szymczyk[2], G. Koeckelberghs[1], R. Verbeke[1], W. Egger[3], I.F.J. Vankelecom[1], H. Mariën*[1]

[1]KULeuven, Belgium, [2]Institut des Sciences Chimiques de Rennes, France, [3]Universitäd Munchen, Germany

Introduction

Nucleophilic ring opening of epoxides with amines already proved to be an efficient interfacial polymerization (IFP) reaction leading to membranes with excellent chemical and mechanical properties. Based on Carothers and Flory-Stockmayer theories, more functional groups on the epoxide or amine monomers could lead to faster gelling, and thus accelerated film formation and more intensified densification to induce higher membrane selectivities. Also, thin-film composite (TFC) membranes were synthesized via anionic ring opening polymerization using an epoxide homopolymerization.

Methods

Different amines, with varying functionalities and properties, are combined with EPON in IFP to form membranes for use in solvent resistant nanofiltration. As for the anionic ring opening polymerization, high permeable, selective layers were prepared through *in-situ* polymerization, initiated at the membrane surface by creating two immiscible liquid phases. One phase inside the support layer contains the initiator while the phase on top of it contains the epoxide monomer.

Results

The amine with the highest functionality, diethylenetriamine (DETA) reached 99% RB retention and 1.79 L m^{-2} h^{-1} bar^{-1} EtOH permeance after 5 min IFP. Comparatively, other amines, like piperazine (PIP), showed similar performance but needed longer IFP, while 1.6-hexamethylenediamine (HDA) formed very dense, hence low-permeance top-layers. When using homopolymerization, a superior chemical stability was proven via treatments in 1M HCl or 400 ppm NaOCl at 60 °C for resp. 1 week and 6 h. An unchanged or even improved membrane performance was observed.

Discussion

The full stability of the obtained TFC-membranes was proven in DMF and, most remarkably, also in 1M HCl. However, they were fully degraded in 0.33 M NaOH due to both support- and top-layer instabilities. Filtration experiments confirmed stability in acidic conditions, despite small retention losses ascribed to swelling. DMF swelled both support and top-layer but to a different extend, consequently generating cracks, hence inducing performance loss in filtrations.

Keywords: Thin-film composite membranes, Interfacial polymerization, epoxide, Solvent resistant nanofiltration

[O7.32]

Preparation of high flux and anti-pollution SPSF/PSF composite membrane

Q. Zhang*, Y. Chen, W. Peng, Y. Wang, Y. Zhao

Beijing OriginWater Membrane Technology Co., Ltd. Bejing, China

Sulfonated polysulfone (SPSF) has good membrane-forming ability, hydrophilic and chlorine resistance, which can be used for the preparation of small pore size ultrafiltration or nanofiltration membrane with excellent pollution resistance and chlorine resistance. In this study, SPSF/PSF composite membrane with MWCO of 1000 Da (CM1000) was prepared by coating a SPSF layer on surface of the PSF flat membrane via the dip-coating method. Effects of different base membrane, DS(degree of sulfonation) of SPSF, concentration of SPSF, low molecular weight additives, dipping time and heat treatment temperature on the performance of SPSF/PSF composite membrane were investigated.

SPSF/PSF composite nanofiltration membrane can be prepared by adding low molecular weight additive A and B to the coating solution. It was found that the pure water flux of membrane can reach 96 L/(m^2·h) under 0.4 MPa at 25 °C and the membrane has good anti-pollution performance. SEM revealed that the membrane surface was very smooth, and the SPSF coating thickness was about 200nm. AFM characterization showed that the SPSF/PSF composite membrane surface roughness Ra was about 10nm, showed smooth surface which was consistent with the result of SEM characterization. The surface water contact angle was in the range of 50-60°, showed good hydrophilicity. The rejection ratio of CM1000 for 500 mg/L Na_2SO_4 solution can reach 90 %. Zeta potential showed that the surface of SPSF/PSF composite membrane was strongly negative and without isoelectric point.

SPSF/PSF composite membrane has excellent performance, can be applied to high salt, high colority, high residual chlorine and high concentration organic water, such as decolorization of high colority industrial wastewater, recovery of organics in the paper industry, separation, purification and concentration of juice or sugar in the food industry, desalination of dye and pigment, purification treatment of surface water and groundwater with low salt and high colority.

Keywords: SPSF/PSF composite membrane, Chlorine resistance, Anti-pollution, High flux

[O7.33]

Sub-8nm polyamide thin film composite membranes for reverse osmosis application

Z. Jiang*, S. Karan, A. Livingston

Imperial College London, UK

Thin film composite membranes comprising polyamide films as separating layers have been widely used in reverse osmosis (RO) applications. These membranes have become the most attractive option for desalination, waste water treatment, and water softening due to the energy efficiency or reverse osmosis compared to other separation techniques such as multiple effect evaporation. Conventionally, polyamide films are fabricated via interfacial polymerisation (IP) between m-phenylenediamine (MPD) in an aqueous phase and trimesoyl chloride (TMC) in an organic phase on an ultrafiltration support. This results in the formation of crumpled polyamide films with apparent thickness in the range of ~50 to 300 nm. Such crumpled features created on ultrafiltration supports present a challenge to investigation of the active thickness of the polyamide layer and to understanding the transport mechanism through the membranes. Here we report sub-8 nm polyamide films fabricated at a free liquid-liquid interface. This leads to the creation of ultra-smooth films with root-mean-square roughness of less than 1 nm (Fig. 1(a)). These free-standing polyamide films were transferred onto various supports to demonstrate the effect of supports on the overall performance of composite membranes. By controlling the interfacial reaction conditions, we manipulated the active thickness of polyamide films down as low as ~6 nm (Fig. 1 (b)). Composite membranes comprising such smooth films exhibit comparable water permeances to commercial and reported RO membranes with crumpled features. Considering that the ultra-smooth surfaces of sub-8 nm polyamide films provide less than o f that water permea han fo al RO membr into th posite membr date in ns for desalin

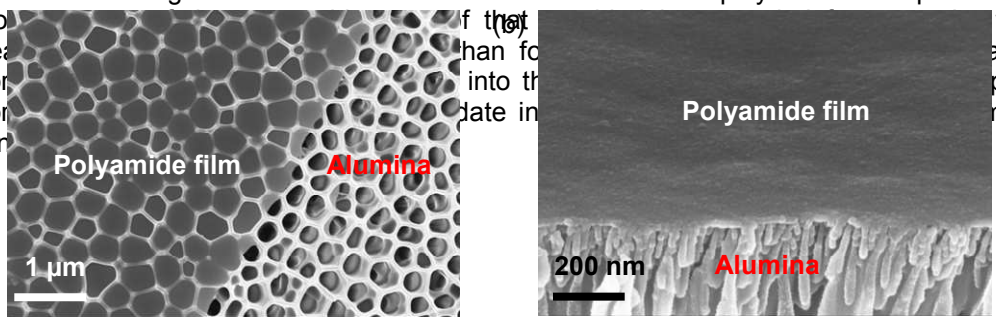


Figure 1: SEM (a) surface and (b) cross-sectional images of ultrathin and smooth polyamide films on alumina supports.

Keywords: Ultrathin films, Free-standing polyamide films

[]

Real-Time Control of Energy-Optimal Operation of Two-Stage RO Desalination

L.X. Gao*, A. Rahardianto, P.D. Christofides, Y. Cohen
UCLA, USA

A novel two-level model-based control approach was developed for energy-optimal operation of a two-stage RO membrane desalination. The control approach was formulated based on the specific energy consumption (SEC) analysis framework for a two-stage RO desalination system accounting for pump efficiencies, various physical system constraints and temporal variability of feed salinity. This SEC framework was then implemented as a higher-level (supervisory) control system for real-time optimization of the RO SEC. A supervisory controller utilized real-time plant data obtained from plant sensors and an SEC model of two-stage RO operation to determine the energy-optimal water recovery for the overall system (Y) and the first-stage (Y_1) for a given water productivity target, feed salinity, and membrane permeability. The derived operating state was then applied through a lower-level control system consisting of three separate feedback loops regulating the RO feed flow rate, the first-stage RO pressure, and the second-stage RO pressure through the actuation of the first-stage RO feed pump, the second-stage RO feed pump, and the RO concentrate valve, respectively. The two-level control system was implemented and demonstrated in a brackish water desalination plant capable of permeate productivity up to 40,000 gallons/day. Field of brackish water desalination demonstrated excellent simultaneous control of the dynamically coupled control variables and energy-optimal operation.

Keywords: Reverse Osmosis, Energy, Process Control, Process Optimization

[O7.35]

Pilot-scale chlorination of BW30 TFC membranes and their thorough physico-chemical characterization

R. Verbeke*[1], V. Gomez[2], W. Egger[3], A. Bergmaier[3], I.F.J. Vankelecom[1]

[1]KU Leuven, Belgium, [2]Dow Water and Process Solutions, Spain, [3]Universität der Bundeswehr München, Belgium

Chlorination remains a big hurdle in membrane technology as the most commonly used membranes for water purification consist of a polyamide (PA) top layer, which is not resistant towards chlorine-induced oxidation (**Figure 1**). Contradicting lab-scale experiments prove that the exact effect on membrane integrity and performance remains unclear. Besides, only one pilot-scale study has been reported so far, which did not completely mimic industrial conditions. To bridge the gap between accelerated lab-scale chlorination and the accidental chlorination in a water-treatment plant, we herein report the systematic investigation of the effect of sodium hypochlorite (NaOCl) on a PA membrane under industrial conditions. BW30 membrane modules were chlorinated with NaOCl (from 0 to 50ppm) for 2h at pH4 under 10bar at pilot-scale. Their filtration performance showed a proportional increase in rejection and decrease in permeate flow, with increasing chlorine concentration. At 50ppm NaOCl, for example, water flow decreased with 40%, while total ion rejection increased with almost 1%, compared to the non-chlorinated module. The membrane physico-chemical properties were analysed by, amongst others, ATR-FTIR, XPS, XRF and SEM. A proportional decrease in IR PA-peaks together with an increase in incorporated chlorine was observed with increasing chlorine concentration, while the typical PA structure remained present. Positron annihilation lifetime spectroscopy (PALS) revealed a decrease in the PA free-volume hole size as chlorine concentration increased, evidencing that the free-volume hole radius is an important parameter governing transport through the membrane active layer. Elastic Recoil Detection (ERD), applied for the first time ever on TFC PA membranes, provided extra information on the elemental composition, including hydrogen, of the membrane sample as function of depth.

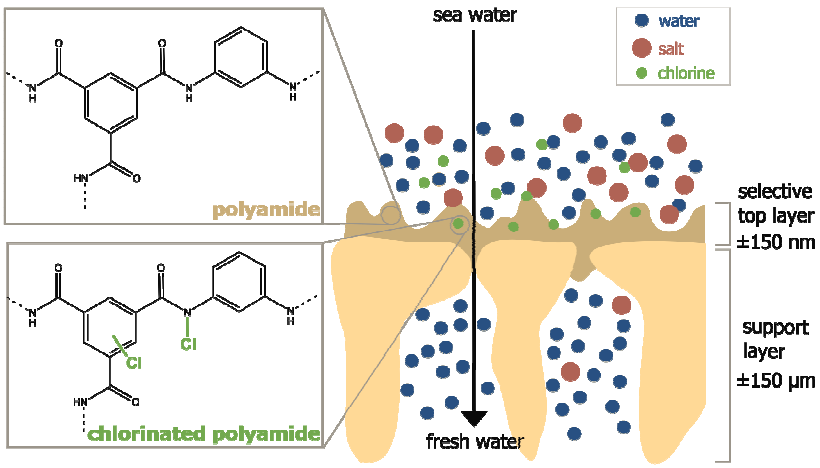


Figure 1: Basic scheme of a reverse osmosis membrane separation process. The top layer typically consists of PA, which is susceptible to chlorine attack. Membrane chlorination eventually results in a performance decline.

Keywords: polyamide, pilot-scale chlorination, novel characterization tools, PALS

[O7.36]

Development of robust reverse osmosis (RO)/nanofiltration (NF) membranes with thermal stability and chlorine tolerance and application to various types of water resources

T. Tsuru*[1], J. Ohshita[1], W. Nishijima[1], M. Hirose[2], T. Tsustsumi[3], G. Gong[1], W. Puthai[1], S.M. Ibrahim[1], H. Nagasawa[1], M. Kanezashi[1]

[1]Hiroshima University, Japan, [2]Nitto Denko Corporation, Japan, [3]Fukuyama City University, Japan

Polyamide thin-film composite (TFC) membranes currently dominate the commercial market of reverse osmosis (RO)/nanofiltration (NF). However, polyamide TFC membranes are quite susceptible to chlorine, and can be used only in a limited range of temperature. In CREST project (the Core Research for Evolutional Science and Technology), robust RO/NF membranes that can be used for water containing chloride and water in a wide pH range and/or at high temperatures have been successfully prepared from polyamide as well as sol-gel derived ceramic membranes.

In this presentation, the concept of ROBUST RO/NF membranes for various types of water, and development of several types of ROBUST membranes made from polyamide and ceramic, and application to field test will be introduced.

Polyamide RO/NF membranes with chloride tolerance have been developed. Application to filed test using 4-inch modules confirmed excellent tolerance to continuous injection of 10-100ppm chlorine as long as half a year, which was equivalent to CT value of 120,000 ppm h.

Two types of ceramic RO and NF membranes were successfully prepared from organosilica derived from bridged alkoxysailanes such as bis(triethoxy silyl)ethane (BTESE) and metal oxides such as SiO_2-ZrO_2, respectively. BTESE-derived organosilica membranes showed high rejection for NaCl higher than 99 %, and low molecular weight cut-offs of 60-80, which is equivalent to seawater desalination membranes, were confirmed to show excellent chloride tolerance and thermal stability upto 90°C.

SiO_2-ZrO_2 nanofiltration membranes with molecular weight cut-off of several hundreds were successfully prepared with different Si/Zr compositions (10/0, 5/5, 8/3, 0/10). SiO_2-ZrO_2 membranes with Si/Zr of 5/5 showed stable performance at 90°C as long as 100h, and in a wide range of pHs (1-13). In addition, SiO_2-ZrO_2 nanofiltration membranes were tuned to show low molecular weight cut-offs less than 200.

We believe robust RO/NF membranes will simply conventional membrane-based processes and create new processes.

Keywords: robust reverse osmosis, robust nanofiltration, polyamide, organosilica

[O7.37]

What makes the polyamide desalination membranes so unique: New insights into membrane structure and ion rejection mechanism

N. Fridman-Bishop*, V. Freger

Technion-Israel Institute of Technology, Israel

Polymeric aromatic membranes are widely used for salt removal, but curiously only very few materials have been found selective and permeable enough to make successful RO membranes, most notably, aromatic polyamides (PA) and cellulose acetate (CA). It was suggested that low dielectric properties combined with presence of multiple hydrogen-bonding sites could be key to achieving both high salt rejection and reasonable water permeability, yet many questions remain.

The present study uses electrochemical impedance spectroscopy (EIS) to directly measure polymer permeability to ions in single salt solutions without any water flow, in order to reveal features that make polymeric aromatic membranes unique.

EIS results of a RO membrane show strong deviations from the standard exclusion mechanisms in nanopores, with much lower conductivity and different scaling behavior, controlled by proton uptake. In addition, EIS results of a neutral dense polyamide membrane show similar scaling behavior with much lower conductivity.

Combination of both results indicate the membrane has a sponge-like structure containing water filled voids separated by thin sub-10 nm films of Nomex. This special structure, resulted from the interfacial polymerization process, enables the combination between the extremely high salt exclusion caused by the dense polymer, with high water flux related to the effective small thickness and high membrane strength.

In addition, combining the high proton permeability found and it's commonly low concentration in most real life application results in an interesting interplay between protons and ions rejection. On one hand trance membrane potential, built mainly by salts presents in the solution effect the protons due to their high permeability value. And on the other hand, high protons concentration inside the membrane may both enhance and suppress salt permeation even at close to neutral pH values. Both effects will be discussed and consequences on real-life applications will be examined in the presentation.

Keywords: Electrochemical impedance spectroscopy (EIS), ion transport mechanism, random-resistor network, Reverse osmosis

[O7.38]

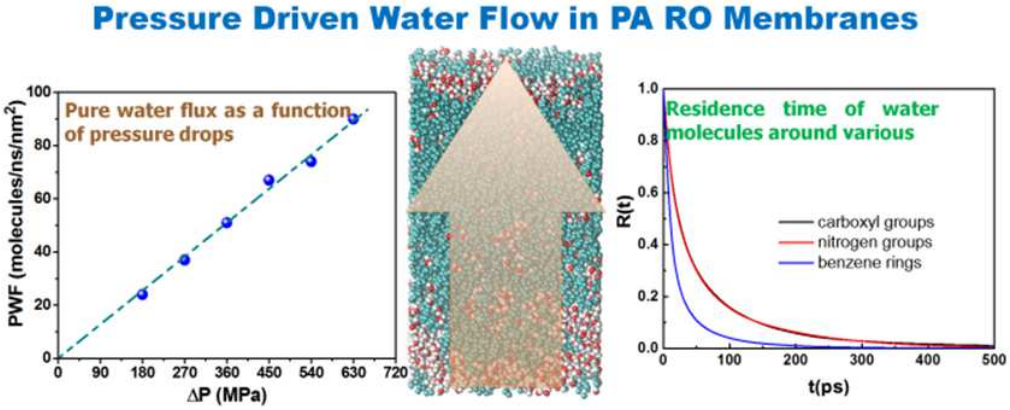
Water flow inside polyamide reverse osmosis membranes: A nonequilibrium molecular dynamics study

Y. Song*, F. Xu, M. Wei, Y. Wang
Nanjing Tech University, China

Among all desalination technologies, reverse osmosis (RO) technology is the most widespread technology to obtain the freshwater capacity. To further enhance the water flux of RO membranes, it is important to understand the molecular mechanism of water transport through the membrane. We apply a steady state nonequilibrium dynamics simulation (SS-NEMD) to study the behavior of water molecules flowing inside the RO membranes, by directly applying external forces on the water molecules to simulate pressure drops, since the mass transport resistance inside the membrane is what we mostly considered.

Before measuring the relationship between pressure drops and the pure water flux, we estimated the average density along z direction of simulation boxes and pore size inside the membrane, which is in good consistency with the experimental values. Then, six pressure drops were applied on water molecules to investigate the e□ect of pressure drops on the pure water flux (PWF). In each pressure drop, there is no obvious tendency of continuous increase or decrease in the PWF, we believe the simulation reached steady states. From the six pressure drops, it is obvious that the water flux increases almost linearly with pressure drops despite small fluctuations due to the random thermal motion. From that, we could calculate the water flux at the experimental condition. At last, we revealed the interactions between water molecules and functional groups. We find that, water molecules move faster around benzene rings than do around carboxyl or amino groups in the membrane.

In this work, the results confirm that RO membranes containing more benzene rings would reduce the mass transport resistance of water inside the membranes. These findings are expected to increase our understanding on the water transport behavior in RO membranes and also the rational design of advanced RO membranes with upgraded permeance.



Keywords: confinement effect, molecular simulation, non-equilibrium molecular dynamics, reverse osmosis

[O7.39]

In situ biofouling investigation in spacer-filled channel using Optical Coherence Tomography (OCT)

L. Fortunato*, T. Leiknes

King Abdullah University of Science and Technology (KAUST), Saudi Arabia

Introduction

The use of optical coherence tomography (OCT) to investigate biofilms in membrane systems increased with time. OCT is able to characterize *in-situ* and non-destructively the biofilm. In this study two different methods involving the analysis of 3D OCT in spacer filled channel systems are proposed and evaluated. The approaches allow obtaining the spatially-resolved and time resolved structural information of a biofilm. The biofilm development in a flow cell containing a membrane and feed spacer was monitored to evaluate the suitability of the proposed approaches.

Materials and Methods

At a fixed position of the flow cell, a volume of 6 × 6 × 0.95 mm^3 was periodically scanned. The total biomass volume was divided into three sub-volumes to assess biofilm distribution over the flow cell elements: membrane, spacer and glass. This study demonstrated that 3D image reconstruction and 3D mapping is also capable of extracting biofilm structural data, enabling to gain information about biofilm growth.

Result and Discussion

The results presented in this study are in agreement with literature, showing that the feed spacer plays a key role in biofouling development in spiral-wound membrane systems. As shown in Figure 1, the biofilm at the initial stage accumulated mainly on the feed spacer. The OCT 3D reconstruction and biofilm thickness map are useful tools to characterize biofilm growth and spatial distribution in membrane systems. The 3D map enables the quick evaluation of a fouled area and can be extend to any surface.

Moreover, a correlation between membrane performance decline and biofilm development was observed after analysing pressure drop increase measurements and OCT scans. The OCT scans can help to determine the impact of different operational parameters (i.e. cross flow velocity, feed pressure and permeate flux) on the overall performance of the filtration processes.

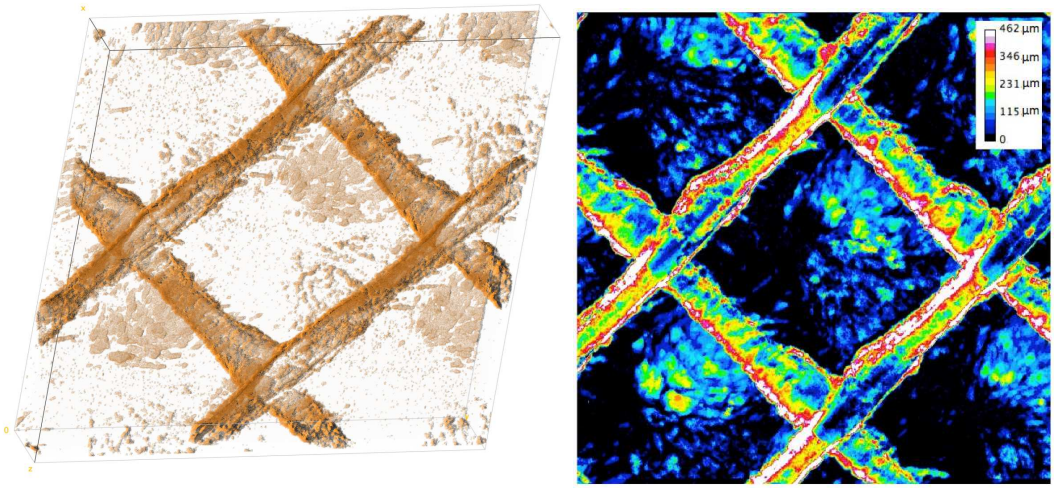


Figure 1. 3D OCT rendered biomass and 3D thickness map at a fixed area of interest (6 mm × 6 mm) in the flow cell.

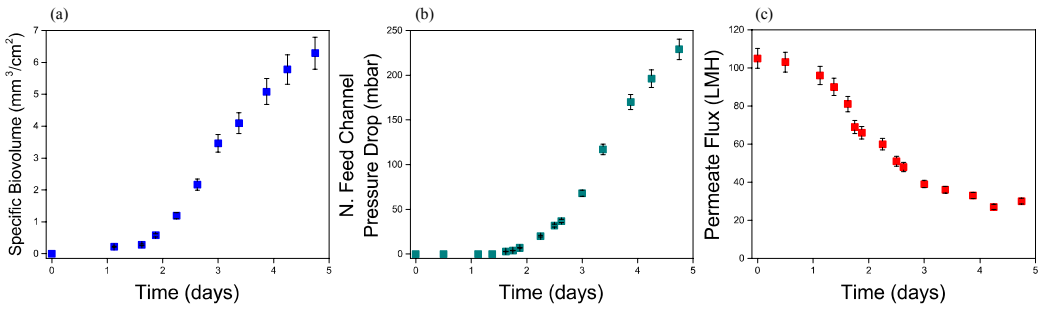


Figure 2. Development of biomass and membrane performances over time. (a) Specific biovolume calculated from the OCT scans. (b) Normalized pressure drop over the MFS feed channel due to biomass development. (c) Permeate flux.

References

[1] L. Fortunato, S. Bucs, R. V. Linares, C. Cali, J. S. Vrouwenvelder, T. Leiknes, Spatially-resolved *in-situ* quantification of biofouling using optical coherence tomography (OCT) and 3D image analysis in a spacer filled channel, J. Memb. Sci. 524, (2017) 673–681.

[2] Fortunato, L., Leiknes, T., 2017. In-situ biofouling assessment in spacer filled channels using optical coherence tomography (OCT): 3D biofilm thickness mapping, Bioresour. Technol. 229, (2017) 231-235. doi:10.1016/j.biortech.2017.01.021

Keywords: Biofouling, Spacer-filled channel, Fouling Monitoring, Feed Spacer

[O7.40]

Visualizing concentration polarization - a new method for in-situ measurement in RO/NF

O. Jung*, F. Saravia, M. Wagner, S. Heißler, H. Horn
Karlsruhe Institute of Technology (KIT), Germany

Scaling is a major drawback in membrane desalination and often determines the limit of recovery. One of the main factors contributing to scaling formation is the phenomenon of concentration polarization (CP). So far no method exists for in-situ measurement of CP in practical application. This work presents a new method with the potential to accurately measure the CP of sulphate using confocal Raman microscopy.

The Raman activity of sulphate makes it a very suitable test compound. The symmetric S-O stretching has a distinct Raman band at 981 cm^{-1}. The calibration curves show a linear correlation of intensity and concentration. Sulphate in solution can also be differentiated from bound sulphate in scale.

Experiments were carried out using a flat sheet membrane filtration unit suitable for Raman microscopy which resembles a spiral wound module. Different NF membranes were utilized. Feed pressure up to 12 bar and crossflow velocities of 0.01 to 0.2 m/s were investigated. All experiments were carried out with filtered $MgSO_4$ solutions of 5 to 20 g/L sulphate.

Spatially resolved visualization of CP was successfully achieved. However, optical restrictions due to refraction complicate the precise determination of important CP parameters such as boundary layer thickness and wall concentration. Therefore results as depicted in figure 1 were corrected with a function obtained from a background measurement. Additional set-up optimization and calculation functions are being evaluated for data analysis to improve results such as the boundary layer thickness which are not readily extractable from the figure.

This work shows the first attempts in the implementation of this method to measure CP in a practical environment. It presents the challenges, limitations and the potential of using confocal Raman microscopy for measurement of CP.

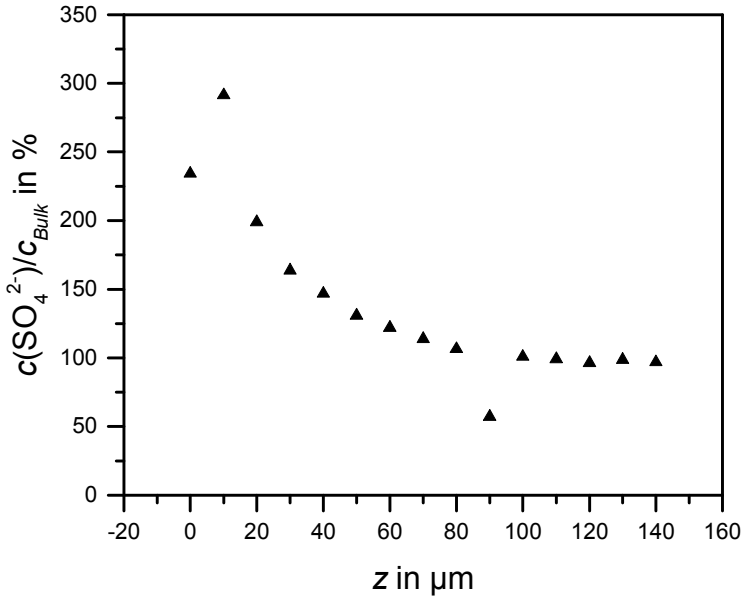


Figure 1: CP of sulphate at p = 10 bar measured with confocal Raman microscopy

Keywords: concentration polarization, reverse osmosis/nanofiltration, confocal Raman microscopy

[O7.41]

Using polytetrafluoroethylene hollow fibers in a gas-liquid membrane contactor for CO2/CH4 separation

J. Ghobadi*[1], T. Lua[1], D. Ramirez[1], R. Jerman[2], M. Crane[2]

[1]Texas A&M University-Kingsville, USA, [2]Eclipse Membranes, USA

Separation of carbon dioxide (CO_2) from a gas stream, using hollow fiber membrane contactors, has been proposed as an alternative technique to conventional processes such as chemical absorption. Experimental measurements of carbon dioxide separation from a gas mixture are presented to confirm the potential of using Polytetrafluoroethylene (PTFE) hollow fibers as a hydrophobic membrane for the removal process. In this study, two types of commercially available PTFE hollow fiber membranes with different inner and outer diameters were employed and compared. The feed gas mixture was composed of 2% CO_2 in balance of CH_4 to simulate the gas stream. The effect of absorbent nature on CO_2 separation was investigated by testing various types of absorbent liquids such as distilled water and aqueous solution of sodium hydroxide (NaOH) and monoethanolamine (MEA). The impact of operational variables such as gas flow rate and flow pattern on the absorption performance of the hollow fiber membrane contactors were also examined. Results indicated that the CO_2 separation efficiency of the membrane modules were inversely proportional to the inner diameter of the PTFE hollow fiber membranes. Additionally, the increase of CO_2 removal form the gas mixture in the case of using amine solution was more pronounced that that obtained with the other types of absorbent liquids.

Keywords: Carbon Dioxide, PTFE Hollow Fiber Membranes, Gas Separation, Absorption

[O7.42]

Recoveries and treatment performance of volatile, semi-volatile, and non-volatile organic contaminants by direct contact membrane distillation

D. Won*[1], E.P. Kolodziej[1,3], K. Salls[2], S.R. Hiibel[2], A.D. Gipe[3], A. Childress[4]
[1]*University of Washington, USA,* [2]*University of Nevada, USA,* [3]*Center for Urban Waters, USA,* [4]*University of Southern California, USA*

Membrane Distillation (MD) is a membrane process capable of targeted separation by hydrophobic membranes to enable vapor phase transport through the membrane pore space after evaporation from the liquid phase. Mass transport is thermally-driven, governed by partial vapor pressure difference resulting from a thermal gradient across the membrane, which is the driving force of mass transfer. When considering potential applications, the dynamics of MD separation become more complex because such feed streams contain many semi-volatile and volatile solutes which might be toxic pollutants. For solutes with any degree of volatility, separation performance will be characterized by partial rejection, and even concentration enhancement in the permeate for constituents that are more volatile than water. We evaluated the fate of several dozen non-volatile, semi-volatile, and volatile organic contaminants in a bench scale gas-tight DCMD system.

Mass recoveries of solutes were used to evaluate their mass loss by sorption to the MD system and were well correlated with their hydrophobicity, log Kow. Satisfactory recoveries were determined by a clear distinction near 60% and classified by their chemical groups; good recovery (> 60%; phenols, halogenated phenols, PPCPs, and aromatic amines) and poor recovery (< 60%; halogenated benzenes and PAHs). While non-volatile solutes exhibit near 100% rejection due to their low volatility, rejection of semi-volatiles and volatiles ranged from poorly (-300% to 20% rejection) to well (near 90% rejection) removed, and were not always consistent with metrics of volatility such as Henry's law constant, pKH. Predicting rejection performance can be approximated with chemical parameters such as henry's law constants and vapor pressures, yet the potential for removal in the system also seems to be dependent on other factors in complex feeds. In particular, the ability to define permeate fluxes of solutes calculated by mass-transfer coefficients would be useful to estimate system performance.

Keywords: semi-volatile organic compounds, Direct contact membrane distillation(DCMD), mass recovery, rejection

[O7.43]

Power generation in a reverse electrodialysis system using SWRO brine and sewage-treated water

M. Higa*, T. Sakurada, M. Kuno, M. Yasukawa
Yamaguchi University, Japan

Recently, salinity gradient power (SGP) has regarded as one of sustainable energy resources. The SGP generates when two salt solutions with different salinity are mixed. A reverse electrodialysis (RED) system uses cation exchange membranes (CEMs) and anion exchange membranes (AEMs) to change SGP into useful electricity. There have been many studies on the evaluation of power generation using small RED stacks. However, to the authors' best knowledge, there have been no study on power generation of a pilot scale RED system using brine from a seawater desalination reverse osmosis (SWRO) plant and sewage-treated water from a sewage treatment facility. The aim of this study is to evaluate the power generation properties of a RED system with 40 m^2 of total membrane area using SWRO brine (SB) and sewage-treated water (TW).

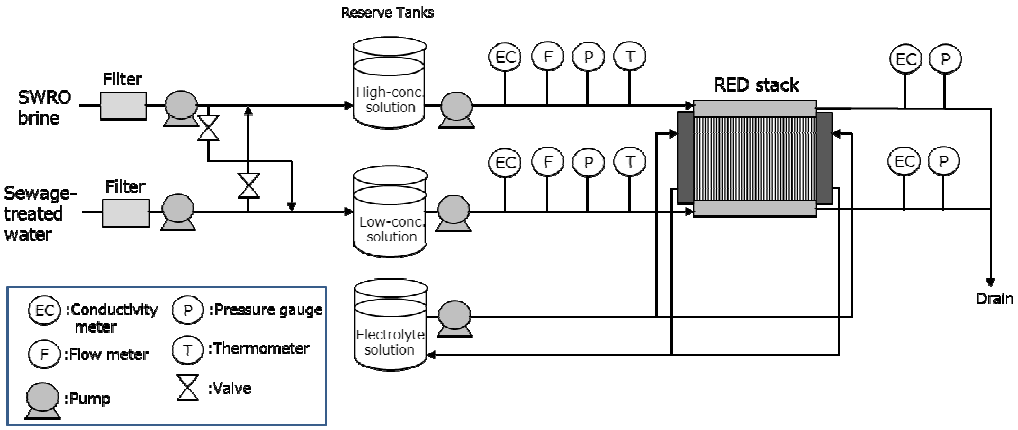


Fig. 1. Flow diagram of the RED system in this study.

Figure 1 shows flow diagram of the RED system in this study. The RED stack used in this study consisted of 200 pairs of power generation cells that had a CEM, an AEM and two flow channels for SB and TW. Neosepta® CMX and AMX (Astom Co. Japan) were used as the CEM and AEM, respectively. The effective membrane area of each membrane was 1000 cm^2 (20 cm X 50 cm).

Figure 2 shows gross power, net power and pumping energy of the RED system as a function of flow rate of SW and TW. The gross power increased with increasing flow rate, and showed 21.7 W at 8.4 L/min of the flow rate. Since pumping energy also increased as the flow rate increased; hence, the net power had a maximum value of 18.2 W at 4.3 L/min of the flow rate.

From the results, an RED system using SWRO brine and sewage-treated water will have potential application as an energy generating system.

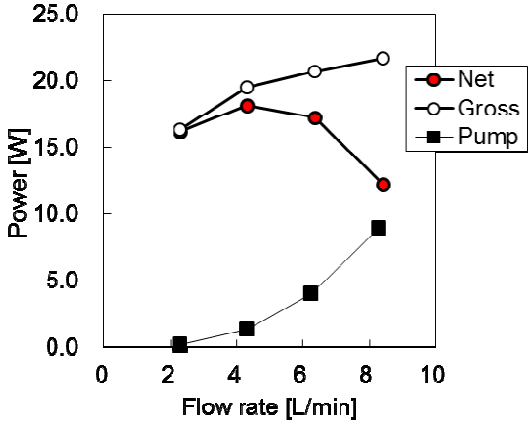


Fig. 2 Gross power, net power and pumping energy of the RED system as a function of flow rate of SW and TW.

Keywords: Reverse electrodialysis, salinity gradient power, SWRO brine, sewage-treated water

[O7.44]

Effect of flow rate, bulk temperature, and channel depth on flux in nanophotonics-enhanced solar membrane distillation

S.S. Pedersen*, A.A. Alabastri, P.D. Dongare, Q. Li
Rice University, USA

Nanophotonics-enhanced solar membrane distillation (NESMD) is a novel modification of the traditional membrane distillation (MD) process, utilizing low-cost carbon black nanoparticles to efficiently convert absorbed sunlight into heat directly at the membrane surface. Because of the unique direct surface heating configuration of NESMD, optimum operational parameters will be different from traditional MD. In this study, we explore the effect of varying feed/permeate flow rates, bulk temperatures, and channel depths on the flux in NESMD.

Bench-scale experiments using simulated sunlight were performed to determine the effects of these operating parameters. Three-dimensional finite element modelling of the NESMD system was performed using COMSOL Multiphysics software, and simulations run to validate the experimental results.

Our work shows that flux is maximized as feed flow rate decreases and permeate flow rate increases. This is in contrast to traditional MD where flux decreases with decreasing feed flow rate due to temperature polarization. For a given temperature difference, we show that flux increases as the bulk feed/permeate temperatures increase. Flux also increases as the feed channel depth decreases and the permeate channel depth increases. The relationships between heat transfer, flow rate, and channel geometry suggest the use of dimensionless design parameters, such as the Reynolds, Peclet, Nusselt, or Prandtl numbers to characterize performance of the NESMD system.

Keywords: membrane distillation, nanophotonics, flow rate, modeling

[O7.45]

Impact of module size on performance of renewable energy powered membrane system

A.I. Schaefer*, A. Jeihanipour, J. Shen, B.S. Richards
Karlsruhe Institute of Technology (KIT), Germany

Integration of renewable energy (RE) and membrane technology to provide a sustainable drinking water supply have been successfully tested and to some extent implemented in remote areas, where access to energy grids as well as potable water sources is limited. Spiral wound (SW) elements of reverse osmosis (RO) and nanofiltration (NF) membranes are the most common in water treatment. For small scale decentralised systems with direct renewable energy coupling, energy fluctuates and with this transmembrane pressure and feed flowrate. This raises the question if one 4'' or three 2.5'' membrane modules (same membrane area) are providing better performance.

To investigate the impact of module size on variation of permeate flux, retention and specific energy consumption (SEC), a pilot-scale reverse osmosis solar installation (ROSI) was used in remote areas under fluctuating solar conditions. The RE-membrane system consisted of two stages, ultrafiltration (UF) pretreatment followed by NF/RO, using NF270 and BW30 modules. Two different configurations were investigated, firstly one 4" NF/RO module, and secondly three 2.5" modules in series. A high fluoride content brackish water from Mdori borehole, in a remote village near Lake Manyara (Northern Tanzania), was treated with a of 5.5-6.0 bar and 600 L/h feed set point.

The BW30 membrane produced a better permeate water quality (meeting the WHO fluoride guideline) but lower permeate flux and significantly higher SEC compared to the NF270 membrane. For both membranes the first and second 2.5" modules showed a better performance in terms of permeate flux, SEC and recovery than the 4" module while the last 2.5" affected performance negatively. The main difference in hydrodynamic conditions was the crossflow velocity which was higher in module 1 and 2 of the 3×2.5" modules and resulted in a lower concentration polarization. However, the overall performance of the 3×2.5" configuration did not improve predominantly because of the poor performance of the last module.

		
System testing in field lab with different module sizes	Mdori water source, Tanzania with about 50-60 mg/L fluoride	Field testing at the multi-purpose Mdori Water source

Keywords: fluoride, brackish water desalination, solar energy, nanofiltration & reverse osmosis

[O7.46]

Using green solvent, triethyl phosphate (TEP), to fabricate highly porous PVDF hollow fiber membranes for membrane distillation

J. Chang*[1], J. Zuo[1,2], L. Zhang[3], T.S. Chung[1]

[1]National University of Singapore, Singapore, [2]Singapore Institute of Technology, Singapore, [3]Institute of High Performance Computing, Singapore

While membrane technology continues to thrive in seawater desalination, it would defeat the very purpose of saving the environment if toxic solvents are involved in membrane manufacture. As a paradigm of green chemistry, a non-toxic solvent, triethyl phosphate (TEP), was used for the first time to fabricate polyvinylidene fluoride (PVDF) hollow fiber membranes for direct contact membrane distillation (DCMD). The phase inversion kinetics of the PVDF/TEP system was closely investigated and compared with the conventional N-Methyl-2-pyrrolidone (NMP)/PVDF system. The former showed a less abrupt phase inversion rate and produced a more porous sponge-like structure than the latter. The 12/88 wt% PVDF/TEP binary solution produced fibers with promising performance. They not only possessed robust mechanical properties and a liquid entry pressure up to 2.0 bar but also exhibited an average flux of 20 $kg/m^2 \cdot h$ at 60 °C and a NaCl rejection of 99.99%. In addition, hollow fiber membranes spun from this PVDF/TEP system had porosity of greater than 83% for all conditions studied. Since there were no additives or non-solvents in the dope solutions and no post-treatments involved, the use of TEP as a green solvent could significantly reduce the complexity of membrane fabrication, scale up and commercialization. Clearly, the much safer solvent TEP is able to replace toxic solvents commonly used in membrane manufacture and to produce membranes with highly competitive performance.

Keywords: Triethyl phosphate, Green Solvent, PVDF hollow fiber membranes, Membrane distillation

[O7.47]

Construction of sulfonate polyelectrolyte complex nanoparticles and application as membranes

Q.F. An*[1,2], P.Y. Zheng[2], C.C. Ye[2], N.X. Wang[1]

[1]Beijing Key Laboratory for Green Catalysis and Separation, College of Environmental and Energy Engineering, Beijing University of Technology, China, [2]MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science & Engineering, Zhejiang University, China

Polyelectrolyte complexes (PECs) are formed through the electrostatic complexation of oppositely charged polyelectrolytes. Owing to ionic cross-linking structure and free charged groups, PEC membranes (PECMs) have already been utilized in pervaporation, nanofiltration and fuel cells. However, weak polyacid based PECs commonly suffer from poor mechanical properties and separation performance of membranes owing to weak ionic interactions and hydration ability. In this work, we engineer strong polyacid based PECs (SPECs) nanoparticles featuring sulfonate ionic cross-linking and free sulfonate groups through a conceptually novel strategy of “complexation-sulfonate”. In detail, chitosan (CS) and strong polyacid containing SO_3^- groups are solution-mixed to prepare PECs. Subsequently, through the sulfation of residual NH_2 groups on CS, the PECs are modified with free SO_3^- groups, followed by solution casting to fabricate SPECMs. According to mechanical strength test, mechanical properties of SPECMs are enhanced to a level that could compete with hybrid films, with tensile strength and elongation at break reaching as high as 108.3 MPa and 5.0%. Besides, when applied in pervaporation of dehydrating 10 wt% water/ethanol mixture at 70 ^oC, the flux and water content in permeate are 1980 g m^{-2} h^{-1} and 99.55 wt%, respectively. Moreover, SPECMs also achieve a water permeability of 6.71L m^{-2} h^{-1} bar^{-1} in nanofiltration, together with the selectivity for NaCl/Na_2SO_4 and NaCl/methyl blue dye separation being as high as 13.1 and 850.0, respectively. Being a novel membrane building block, hydrophilic SPEC nanoparticles reduce transfer resistance and promote fast transport of water molecules, resulting in SPECMs with remarkable separation performance applied to pervaporation and nanofiltration.

Keywords: polyelectrolyte complexes, pervaporation, nanofiltration

[O7.49]

Novel supported liquid membranes with liquid ionic as carrier for metal ions extraction

L. Lebrun*[1], E. Jean[1], D. Villemin[2]

[1]University of Rouen, France, [2]ENSICAEN, France

Introduction

Supported liquid membranes (SLM) have many attracted assignments but their industrial applications are limited because of their instability. The use of high hydrophobic carriers could improve the stability of the SLM during the process. In the present work, the approach was to use ionic liquids (IL) as carriers with anions, known as efficient carriers for metal ions extraction and containing long fluorinated chains to improve the interactions with the support membrane.

Methods

Novel IL were first synthesized and purified: isooctylmethylimidazolium bis-2-ethylhexylphosphate ($iOMim^+$ $D2EHP^-$) and 1-butyl-3-decylimidazolium di-1-H,1-H,2-H,2-H-perfluorodecylphosphate ($C10BIm^+$ $PFC10^-$). The SLM was made of a micro-porous polyvinylidenedifluoride supporting membrane impregnated with a 0.1 mol L^{-1} of IL in dodecane. The transport experiments were performed on heavy metal ions Hg(II), Cd(II), and Cr(III) and on rare earth ions Eu(III), Nd(III), Y(III) and Yb(III). The transport of the ions was modelled in studying the influence of the carrier, ions concentration, pH and temperature.

Results

SLMs were very permeable for ions, especially for Hg(II) and Nd(III). Transport properties were highly influenced by pH and by the hardness of metal ions and carriers. Indeed, hard anions ($PFC10^-$) and ($D2EHP^-$) form very stable complex with hard metal ions Yb(III) and Cr (III) that are less easily dissociated for diffusion. The diffusion of ions was faster with ($C10Bim^+$ $PFC10^-$) than with ($iOMIm^+$ $D2EHP^-$) carrier due to a difference in the mechanism: by jumping from site to site for the first and by vehicular type mechanism for the second. The strategy for stabilizing the SLM by using fluorinated LI was effective, because the membrane containing ($C10BIm^+$ $PFC10^-$) carrier leached only 5 % of LI after four consecutive diffusion experiments.

Conclusion:

SLMs containing high hydrophobic IL as carrier were successfully used for the extraction of soft metal ions. Such LI responds to the lack of stability of SLMs.

Conclusion

We clearly outlined the influence of the ion's hardness and the carrier's structure.

Keywords: Supported liquid membrane, Ionic liquid, Heavy metal ions, Rare earth ions

[O7.50]

High performance facilitated transport composite membranes for real industrial olefin/paraffin separation

R. Zarca, M. Fallanza, A. Ortiz*, D. Gorri, I. Ortiz
University of Cantabria, Spain

Separation of olefin/paraffin gas mixtures from refinery processes off-gases has been traditionally performed by cryogenic distillation, which is a highly capital and energy intensive operation. To overcome this handicap, process intensification through facilitated transport composite membranes is proposed.

In this work, we report the utilization of polymeric facilitated transport composite membranes integrating the use of PVDF-HFP polymer, $BMImBF_4$ ionic liquid and $AgBF_4$ salt. These membranes exploit the Ag^+ capability to selectively and reversibly react with the olefin, enhancing its permeability. The ionic liquid is used as membrane additive because it provides stability to the metallic cation dissolved inside, acting as a medium for facilitated transport with mobile carrier [1,2].

Gas mixture permeation experiments were conducted at several experimental conditions and membrane compositions to determine the selectivity and permeability of the gaseous species. Furthermore, in order to assess the separation performance and the stability of the membrane under real conditions, real gas mixtures provided by a refinery were tested as well.

Finally, a simple yet effective mathematical model for the permeation process is proposed. The model is able to calculate the olefin flux through the membrane as a function of the operating conditions and membrane composition by considering the various transport mechanisms taking place in the permeation process. The reported model is a very useful tool for process optimization and scale-up.

References

1. Ortiz A., L.M. Galán, D. Gorri, A.B. De Haan, I. Ortiz, Kinetics of reactive absorption of propylene in RTIL-Ag^+ media. Separation and Purification Technology, 2010. 73(2): p. 106-113.

2. Fallanza M., A. Ortiz, D. Gorri, I. Ortiz, Polymer–ionic liquid composite membranes for propane/propylene separation by facilitated transport. Journal of Membrane Science, 2013. 444: p. 164-172.

Acknowledgements

Financial support from the Spanish Ministry of Science under the projects CTQ2015-66078-R and CTQ2016-75158-R (MINECO, Spain-FEDER 2014–2020) is gratefully acknowledged.

Keywords: Real olefin/paraffin gas stream separation, composite membrane, Facilitated transport, modelling

[O7.51]

Olefin gas separations using facilitated transport polymeric membranes

J.R. Klaehn*[1], C.J. Orme[1], A.D. Wilson[1], S. Majumdar[2]

[1]Idaho National Laboratory, USA, [2]Compact Membrane Systems, USA

Olefin production is a multibillion dollar industry that is needed for organic feedstocks in the production of plastics and fuel sources. However, current industrial separations of olefins are done by cryogenic distillation. Most polymeric membranes, by themseleves, are often ineffective in these separations due to low permeabilities and physical similarity between olefin and paraffin gases. Therefore, metal ion facilitators (e.g., Ag^+) are used to provide high selectivity in this difficult separation. Casting a polymeric membrane with embedded Ag^+ facilitators is not well-defined in the literature, but the polymer needs decent permeability for olefin and paraffin gases. We fabricated polymeric membranes at lower silver concentrations than commonly found (~70wt% Ag^+/polymer), and they observe a high olefin selectivity and high permeability. Notably, silver has issues that degrades olefin transport through the membrane and potential metal ion chelate faciliators were synthesized. Overall, a different polymer design and was needed to establish industrial relevance. From our industrial interactions, CMS developed new fluorinated membranes that are stable for long operational periods and olefin separations in challenging feed streams.

Keywords: Olefin/Paraffin Separations, Polymer membranes, Facilitated Transport

[O7.52]

Using a bio-derived solvent to cast polysulfone ultrafiltration membranes

X. Dong*, S. Chede, I.C. Escobar
University of Kentucky, USA

Organic solvents derived from petroleum sources, such as N-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAc), have been traditionally used to fabricate polymeric membranes. These solvents have a negative impact on the environment and human health since most of them are volatile and hazardous; therefore, using renewable solvents derived from biomass is of great interest in order to make membrane fabrication sustainable.

In this study, methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv® PolarClean) was used because it is a bio-derived, biodegradable, nonflammable and nonvolatile solvent. Polysulfone was chosen as the polymer to fabricate membranes due to its thermal stability, strong mechanical strength, good chemical resistance, and antifouling properties. The thermodynamics aspects of the polysulfone/PolarClean/water system were investigated. From cloud point curves and theoretical predictions, PolarClean showed the potential to be a better solvent for polysulfone, and dope solutions could be prepared at a reasonable temperature of 65 □. Polysulfone membranes prepared with PolarClean were also investigated in terms of their morphology, porosity, water permeability, protein rejection and compared with the membranes prepared with traditional solvents. The pores of polysulfone/PolarClean membranes were sponge-like, which led to low water flux and high solute rejection, while those of polysulfone /NMP or polysulfone /DMAc membranes were finger-like macrovoids that led to high water flux and low solute rejection. The water flux of polysulfone/PolarClean membranes was 26.2 LMH, which was lower than polysulfone/DMAc membranes (146.9 LMH) and polysulfone/NMP membranes (48.9 LMH). However, BSA rejection rate using polysulfone/PolarClean membranes reached 92%, which was similar to polysulfone/NMP membranes (93%) and higher than polysulfone/DMAc membranes (86%). The difference of water flux and the solute rejection rate data likely corresponded to their morphologies. In conclusion, bio-derived solvents should be investigated further and may become promising replacements to traditional solvents.

Keywords: ultrafiltration, bio-derived, solvent, sustainable

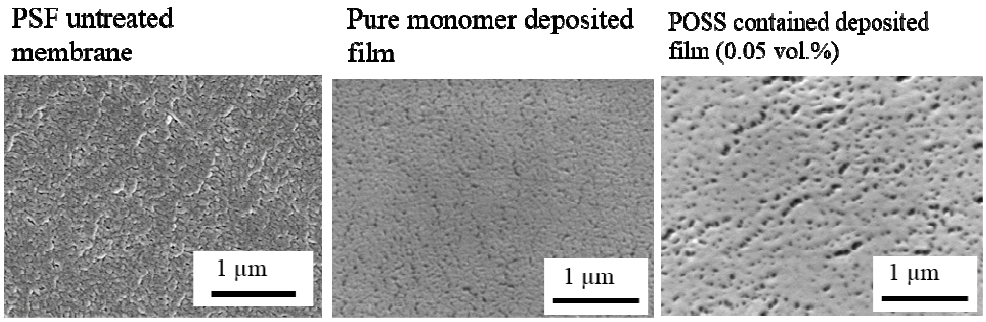
[O7.53]

Aerosol-assisted plasma synthesis of ultra-thin composite membranes for solvent separation

X. Chen[1], Z. Chen[1], C. Laporto[2], R. d'Agostino[2], K. Magniez[1], X. Dai[1,3], F. Palumbo[1], L. Dumee*[1]

[1]Deakin University, Australia, [2]University of Bari, Italy, [3]CNR, Italy

Nanocomposite membranes offer advantages towards specific and enhanced diffusion at the interface between particles and the main matrix. However, the fabrication of composite membranes is hindered by numerous challenges, including complex physico-chemical interactions between the membrane components, agglomeration of particles, and clusters/domains formation, reducing the membrane performance, and selectivity. An alternative simple and environmental friendly deposition of thin film from polyhedral oligomeric silsesquioxane (POSS) nano-cage (2 nm is size) nanocomposite using a novel aerosol assisted plasma polymerization system is demonstrated for the design of solvent separation membranes. The deposited films were prepared with octa-methyl POSS nanoparticles and polymerization of hexamethyldisiloxane (HMDSO) across the surface of commercial poly(sulfone) (PSF) supporting membranes. The POSS concentration (i.e. 0.01, 0.05, and 0.1 vol.%) and thickness (i.e. 50, 150, and 300 nm) was controlled to manipulate the free volume and degree of cross-linking between the nano-cages and the matrix. Particularly, the impact of the POSS integration led to Janus type membranes with both hydrophobic and alcoholphilic properties favourable for specific solvent separation. The roughness increased upon plasma polymerization and POSS addition by approximately 30 % due to the seeding generated by the POSS particles. In addition, the dispersion of the POSS evaluated by SAXS/WAXS and XRR was found to be excellent and very small clusters on the order of 10 nm, and corresponding to 4-5 POSS particles, were evaluated from data modelling. The membrane performance has been measured through pure water, methanol and ethanol filtration. The average methanol flux obtained was also found to vary as a function of the POSS content up to 150 LMH at 75 kPa The presence of the POSS promoted methanol and ethanol permeation and reduced water transfer, with relative selectivities ethanol/water up to 4. Mixed solvent separation experiment and pervaporation will also be presented on amino-functionalized POSS composites.



Keywords: plasma polymerization, solvent separation, nanocomposite membrane

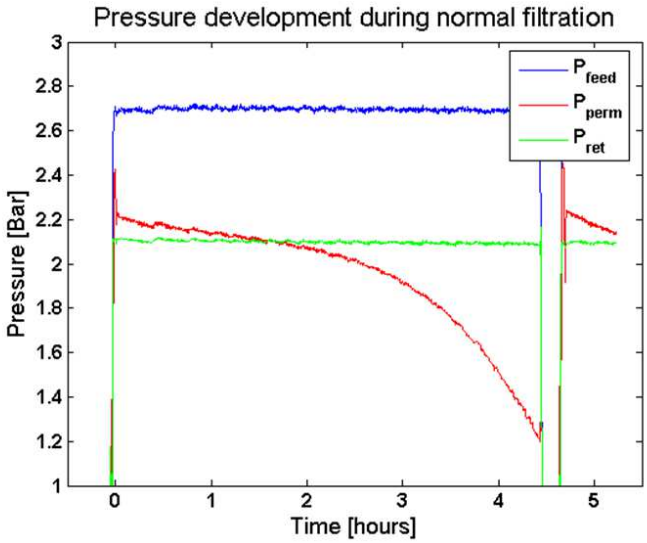
[O7.54]

+Flux a new approach in beer membrane filtration

H.J. Everts*, E. van Mastrigt, R. Folz
Pentair X-Flow, The Netherlands

After the fermenting and cold storage of beer, the beer has to be filtrated in order to remove small particles and yeast that make the beer cloudy. Originally diatomaceous earth (KG) was used for this filter step. In order to reduce the waste streams, hollow fibre micro filtration membranes have been developed for beer filtration. Initially the modules used in the beer membrane filtration (BMF) installation were 750 mm long. In order to change the footprint of the BMF skid, a change had to be made to the modules and process.

Since the crossflow must be high enough in order to prevent preliminary fouling of the membranes and also result in a pressure drop over the concentrate side of the system, modules cannot be made longer in to prevent backflow from the permeate to the concentrate side. This only happens in the beginning of the filtration at a clean membrane where the permeate pressure is higher than the concentrate pressure near the end of the membrane fibre (figure below).



Therefore test have been carried out on longer modules to study the effect of the length of the module on the efficiency and a new way of operating the system was developed. By controlling the liquid level at the permeate side of the module, it is possible to prevent beer from flowing back to the concentrate side of the system while being able to use a longer membrane module. This new way of operating the BMF made it possible to develop modules with a length of 1500 mm, resulting in a reduction of 18 to 6 modules per skid without losing system capacity and reducing the footprint of the BMF skid significantly. Currently the new +Flux system is successfully running at 11 different filtration lines in different breweries.

Keywords: Beer, +Flux, Filtration, Footprint

[O7.55]

GOHAL!: Sustainable membranes for alcohol dehydration

V. Boffa*[1], P.E. Mallon[2], G. Magnacca[3]

[1]Aalborg University, Denmark, [2]University of Stellenbosch, South Africa, [3]Universitá di Torino, Italy

The rise of graphene oxide (GO) has unlocked a new exciting direction in the development of nanofiltration, desalination and pervaporation membranes. However, there are still high concerns about GO at basic pH and under cross-flow conditions. GO stabilization can be achieved by thermal or chemical reduction; but stacked layers of reduced GO (rGO) tend to form ordered and compact graphite-like structures, thus preventing permeation. Here, a humic acid-like biopolymer (HAL), extracted from organic compost with a yield of ~ 20%, was used to fabricate composite GO-HAL membranes [1]. Both GO and HAL consist of a carbon backbone functionalized with oxygen-containing moieties; but GO dispersions are made of 2D layers with monoatomic thickness, while dispersed HAL macromolecules have a 3D branched structure. We fabricated GO-HAL membranes with HAL contents ranging from 0 to 30 w% by the drop-casting method. Upon thermal stabilization, HAL brings a high degree of disorder to the membrane structure, with the benefit of an increased water permeation rate. The membrane with a biopolymer loading of 30% presented an ideal water/ethanol selectivity of 45 and a water permeance that is 33% higher than the pristine graphene oxide membrane. The enhanced water permeability along with the good water/ethanol selectivity makes the GO-HAL membranes promising devices for alcohol dehydration technologies. This study provides a new basis for the rational design of the future generation of GO-based membranes and offers a new perspective in the exploitation of organic urban waste as source of versatile building blocks in the development of new nanostructured membrane materials. This research was made possible by the financial support from the Danish Council for Independent Research (DFF–6111–00151) and by Mat4Treat, H2020-MSCA-RISE-2014 (n. 64555).

[1] V. Boffa et. al., Carbon-based building blocks for alcohol dehydration membranes with disorder-enhanced water permeability, Carbon, *under review*.

Keywords: Graphene oxide, Humic-acid like, Pervaporation, Vapor permeation

[O7.56]

Advances in polymeric membrane preparation using sustainable and green solvents

A. Figoli*[1], T. Marino[1], F. Galiano[1], C. Ursino[1], E. Di Nicolò[2]
[1]*ITM-CNR, Italy,* [2]*Solvay Specialty Polymers, Italy*

Phase inversion (PI) represents a simple and versatile technique adopted to fabricate membranes. This preparation method relies on the phase separation of polymeric solutions allowing a range of different membrane morphology and performance to be produced. However, the main drawback in the extensive use of PI includes the toxicity profile of solvents employed for dissolving the selected polymer [1]. In fact, despite their physical-chemical properties which make of N-methyl-2-pyrrolidone, N,N-dimethylformamide and dimethylacetamide, excellent candidates for preparing polymeric solutions, their (eco)toxicity pose severe risks for human health and the environment [1]. Consequently, the demand for non-toxic and safer solvents for membrane preparation is increasing, due to safety concerns from regulatory restrictions. In accordance with Green Chemistry, membrane technology can improve energy efficiency of industrial processes, allowing green processes development, only if membrane preparation procedure is based on the use of safer solvents and auxiliaries [1]. In this work, Rhodiasolv PolarClean®, an eco-friendly water soluble polar solvent [2,3], is proposed for the first time as alternative solvent for producing polyarylsulfones-based porous membranes. The green solvent ethyl lactate is also proposed as valid substitute of hazards solvents for the preparation of dense poly(lactic acid) (PLA) membranes. With the use of the above more sustainable and greener solvents PES and PLA membrane morphology and performances were tailored by changing the operational conditions. Microfiltration tests demonstrated the applicability of the prepared polyether sulfone porous membranes for water treatments. Dense PLA membranes were efficiently applied in pervaporation for organic/organic separation as methanol from methyl tert-butyl ether.

References

[1] Figoli A., Marino T., Simone S., Di Nicolò E., Li X.-M., He T., Tornaghi S., Drioli E., Green Chemistry, 2014,16, 4034.

[2] www.rhodia.com.

[3] Randovà A., Bartovská L., Morávek P., Matějka P., Novotná M., Matějková S., Drioli E., Figoli A., Lanč, Friess K., J. Mol. Liq., 224, 2016, 1163.

Keywords: Green solvent, Membrane preparation, Porous membranes, dense membranes

[O8.01]

Synthesis of graphene oxide membranes and their behavior in water and isopropanol

A. Aher*[1], Y. Cai[1], M. Majumder[2], D. Bhattacharyya[1]
[1]*University of Kentucky, USA,* [2]*Monash University, Austria*

Abstract:

Graphene oxide (GO) membrane has been synthesized on commercial polysulfone ultrafiltration membranes (Pore size: 17nm) using the drop casting method followed by baking at 90^{o}c for 24 hours. Baking resulted in the reduction of GO and removal of bulk water intercalated in the GO sheets. Deposited GO film showed high stability under shear stress variation. This work shows that water adsorption on the GO membrane determines its permeation performance. Despite the higher viscosity of isopropyl alcohol (IPA), its permeability was 7 times higher than water through the baked ("dry") GO membranes, which were never contacted with water. However, IPA permeability of GO membranes dropped to 44% (of deionized water) when contacted with water ("hydrated" or "wet" GO membranes). Extensive size exclusion (rejection) studies with various dye and dendrimer molecules showed pore size reduced from 3.3 nm in the "dry" state to 1.3 nm in the "wet" state of GO membranes. FT-IR characterization of GO membrane suggested adsorption of water on the nanochannels of the active layer. Also, significant decay in flux was observed for water (82% of its initial flux) as compared to IPA (38% of its initial flux) for initially dry GO membranes [1].

Reference:

[1] A. Aher, Y. Cai, M. Majumder, D. Bhattacharyya, Synthesis of graphene oxide membranes and their behavior in water and isopropanol, Carbon 116 (2017) 145-153.

Keywords: Graphene oxide, isopropanol, solvent, nanoporous

[O8.02]

Carbon Nanotube Hollow Fiber Membranes

R. McGinnis*[1], K. Reimund[2], B. Freeman[2], L. Xia[3], J. McCutcheon[3]

[1]Angstrom Byakuren, USA, [2]University of Texas, USA, [3]University of Connecticut, USA

We report the first carbon nanotube (CNT) hollow fiber (HF) membrane in which the pores of the membrane consist of open nanotubes traversing a non-porous polymer skin. The nanotubes are oriented radially at the surface of the fiber, allowing for outside-in flow with precise size selectivity. Two types of CNT HF membranes will be discussed – membranes using Arc Discharge and CoMoCat nanotubes. Performance data for both water and gas separations will be presented, and this data will be compared to flat sheet CNT membrane data shared previously.

Keywords: Carbon Nanotube Membranes, Hollow Fiber, Water, Gas

[O8.03]

Understanding the interlayer spacing and water properties in graphene oxide membranes

S. Zheng*[1], J. Urban[2], Q. Tu[1], S. Li[1], B. Mi[1]

[1]University of California, USA, [2]Lawrence Berkeley Laboratory, USA

This study presents a novel approach to investigate the interlayer spacing (d-spacing) of graphene oxide (GO) membranes prepared by a layer-stacking method. We developed a combined system of quartz crystal microbalance with dissipation (QCM-D) and in-situ ellipsometer to simultaneously monitor the mass and thickness change of GO membrane in various aqueous solutions, and thus derive the d-spacing and density of GO membrane. When GO membrane swells in aqueous solutions, both the mass and thickness of GO layers increase due to the intercalation of water molecules into the interlayer spaces. For a non-covalent-bonded GO film, we observed severe layer swelling in deionized water, resulting in a drastic increase of the overall thickness and GO interlayer spacing by roughly 10 times. However, dynamic analysis of the GO swelling exhibits an elevated layer density in the initial stage, which was attributed to the increased water density within confined GO layers. We also observed reduced swelling of GO in ionic (e.g. NaCl, Na_2SO_4) solutions compared with that in DI water, due to the dynamic counterbalance between electrostatic/osmotic repulsion and Columbic attraction with the presence of ionic species. A mathematical model was developed to accurately predict the d-spacing of GO membrane based on the aqueous ionic strength. For a covalent-bonded GO film, only slight membrane swelling was observed in deionized water, most likely because of the chain stretching and layer reorganization. Furthermore, molecular dynamics (MD) and density function theory (DFT) simulations of the GO membrane were performed to provide evidence of the proposed swelling mechanisms. The results from this study provide critical information and guidance for improving GO membrane performance in aqueous phase separations.

Keywords: Graphene Oxide, Swelling, Interlayer Spacing, Water Properties

[O8.04]

Positive/negative charge gated ion transport through amine functionalized graphene (AG) nanochannels

X.X. Song*[1], C.Y. Tang[2], C.J. Gao[1]

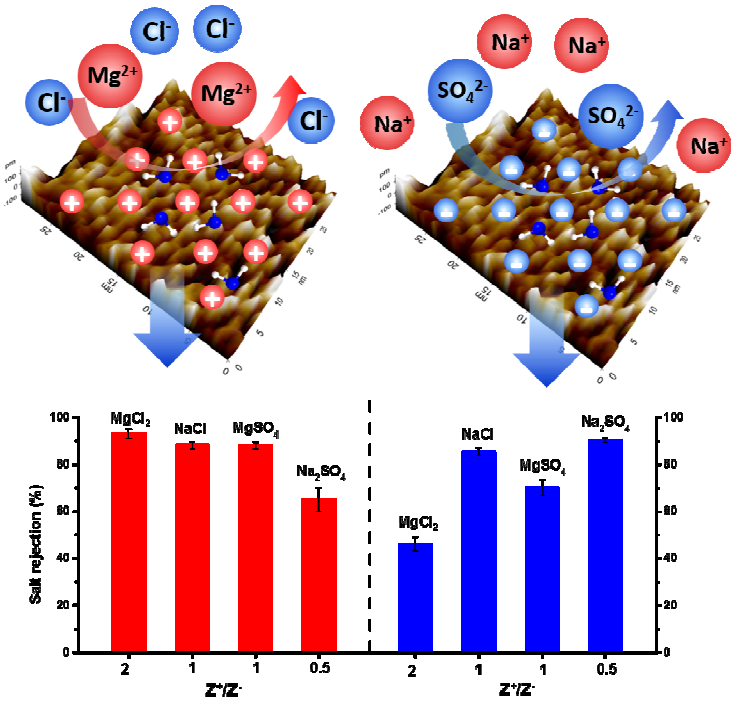
[1]Zhejiang University of Technology, China, [2]The University of Hongkong, Hong Kong

Introduction: Positive/negative charge gated nanochannels have been credited as a highly efficient approach for desalination by mimicking the structure of naturally occurring aquaporin, where size confinement (~0.28 nm at the narrowest spot) and charge exclusion are synergistically combined to achieve molecular sieving. Ideally, the next generation salt rejecting materials for desalination should have more ordered structure, ultrathin thickness, low roughness, and tunable pore size.

Methods: We report for the first time an amine functionalized graphene (AG) membrane framework with positive or negative charge gated '*r*-type' nanochannels. The positive charge is impregnated through a two-step strategy: a) First, GO NSs are sufficiently reduced and grafted with ethylene diamine moieties; b) Next, the surface charge is further enhanced by PAH modification. The surface charge is subsequently altered by NaClO posttreatment to result in negative charged AG membrane. The unique high rejection, low roughness, and charge gated properties of the AG-PAH membrane framework are characterized and analyzed.

Results: When endowed with strong positive charge (4.37 mC/m^2) or negative charge (-4.79 mC/m^2), the AG-PAH nanoporous (average pore radius, r_p ~ 0.39 to 0.54 nm) frameworks show 85%~88% rejection for NaCl, the highest among reported graphene based membranes (GBMs). The classical Hagen-Poiseuille model for the tortuous '*r*-type' nanochannels satisfactorily explain the fast pure water transportation behaviour through the AG-PAH (+) and AG-PAH (-) membranes.

Discussion: An advanced AG-PAH ion-selective separation membrane has been developed with high Na^+ and Cl^- rejection (~ 90%) by the sieving effect through strongly positively or negatively charge gated nanochannels on AG NSs. The charge density and defect radius are identified to be critical determinants to achieve high salt rejection in AG-PAH membranes. This novel design opens avenues to increase NaCl rejection of current GBMs to the level of current RO membranes.



Keywords: Amine functionalized graphene, charge gated nanochannels, nanoporous graphene, donnan exclusion

[O8.05]

Functionalization of graphene oxide with designed polyelectrolyte multilayers architecture

Y. Zhao*[1], K.N. Tang[1], J.F. Pan[1], B.V. Bruggen[2], C.J. Gao[1], J.N. Shen[1]

[1]Zhejiang University of Technology, China, [2]KU Leuven, Belgium

The two-dimensional sheet feature of graphene with its sp^2 hybridized carbon is a hot topic in the fields of materials and chemistry. A major challenge towards the graphene oxide surface activation, sulfonation, grafting, attachment of nanoparticles and surface coating with polymers is the stability. Here, we designed a multilayers architecture of graphene oxide by grafted sulfonation of 4,4' - diaminodiphenyl sulfone (S-DADPS) and reduced in hydrothermal reactor at 180□. The materials have been characterized by Raman, Fourier transformed infrared spectroscopy, X-ray Diffraction, thermogravimetric analysis and transmission electron microscope. The resulting materials thermally stable up to 180 °C and acid stability significantly increased. Furthermore, the excellent ion exchange capacity and conductivity values have been confirmed.

Keywords: graphene oxide, 4,4' - diaminodiphenyl sulfone, Ion exchange capacity, multilayers architecture

[O8.06]

Month-long desalination of cooling tower water with graphene oxide/polymer membranes

L. Biedermann*, M. Hibbs, M. Hightower, C. Mowry, V. Pinon, C. Stewart, M.L. Gucik, K. Zavadil
Sandia National Laboratories, USA

We demonstrated “treat-to-need” tunable desalination of cooling tower blowdown water with graphene oxide (GO)/polymer composite membranes. Thermoelectric power generating impacts 50% of the US freshwater supplies. Increasing the cycles of concentration for cooling water with low-energy desalination technologies will increase the resiliency of power plants to climate change and growing competition for water. To decrease operational costs, membranes should be tolerant to drinking-water level chlorination and resist biofouling and inorganic scaling.

These desalination membranes comprise a laminar GO film covalently bound to a porous polymer support. The laminar GO, covalent linker molecules, and porous polymer support provide enhanced ion rejection, membrane integrity, and mechanical durability. The overlapping GO layers create a two-dimensional, high-flux pathway for water to flow around the individual GO sheets, while blocking the permeation of salt ions. The salt rejection is dynamically tuned by the applied driving pressure, allowing for optimum energy use and treat-to-need water quality.

In partnership with the Electric Power Research Institute (EPRI), we have conducted month-long tests of these membranes against cooling tower blowdown water from three Arizona thermoelectric power plants. The pressure-tunable rejection allows for energy optimization at varying water chemistries. At low pressure (150 psi), scale-forming divalent ions are rejected (80%), while smaller, monovalent ions are partially rejected (eg: 50% for Na). Increasing the pressure to 300 psi significantly increases rejection of the monovalent ions.

The GO/polymer membranes resisted biofilm and inorganic scaling; permeance remained constant over the month-long tests. Crucially, chlorine bleach dosing at 0.5-1 mg/L did not impact rejection or permeance, indicating stability to moderate chlorine levels appropriate for minimizing biofouling.

Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

Keywords: desalination, chlorine-tolerant, graphene oxide, industrial reuse

[O8.07]

2D boron nitride membranes for water separations

Y.T. Chua, J. Ji, D. Mattia*
University of Bath, UK

Boron nitride (BN) is structurally similar to graphene and can be easily fabricated into 2D nanosheets, either single or multi-layered structures, as with its carbon analogue. In addition, the difference in electronegativity between the B and N atoms means that BN could be used for charge-based separations in water or organic solvents. Furthermore, BN has excellent corrosion resistance, high thermal conductivity and chemical and oxidation resistance, which could make it interesting for other separations processes, such as pervaporation.

In this presentation, the preparation of boron nitride nanosheet (BNNS) membranes is reported for the first time. The BNNSs were prepared from hexagonal boron nitride (*h*-BN) powder via microwave-assisted exfoliation in water, followed by fractionation via centrifugation. With this process, stable solutions of BNNSs with controlled thickness in the nm range and average size in the □m range were obtained. The as-synthesized BNNSs were then deposited onto porous organic (PVDF) and inorganic (alumina) commercial substrates by vacuum filtration of the BNNS solution. This led to the formation of a uniform BNNS membrane with controlled thickness and no delamination observed after several wet-dry cycles. AFM analysis of wet and dry membranes on PVDF showed that some swelling of the BNNS membrane occurs when wet under atmospheric pressure.

The pure water permeability of the BNNS membranes was tested showing comparable performance to graphene membranes. Separation of liquids of different polarities and filtration of water with varying salt concentration showed the superior performance of the BN-based membranes in terms of permeability-selectivity behaviour compared to the C-based ones.

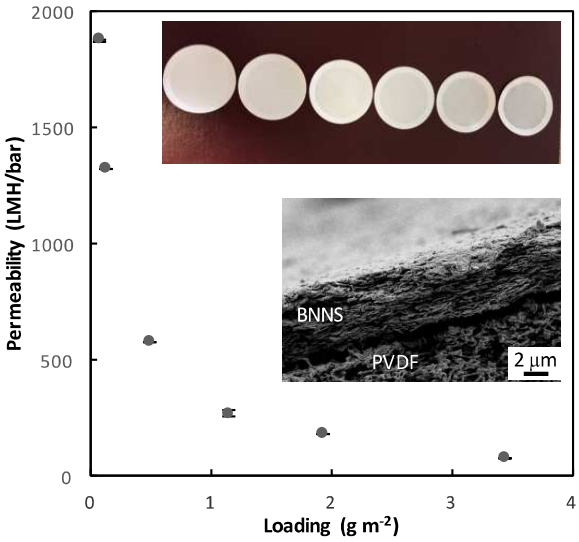


Figure 1: Pure water permeability of BNNT/PVDF membrane as a function of BNNS loading: top inset shows the corresponding membranes, with the colour of the BNNS layer becoming darker as loading increases; bottom inset shows a SEM micrograph of the cross-section of a BNNS/PVDF membrane showing the layered BNNS structure.

Keywords: boron nitride, 2D membranes, water permeability, boron nitride nanosheet

[O8.08]

Highly stable MoS_2 lamellar membrane for selective molecular transport and HER

M.M. Deng*, H.G. Park

ETH Zurich, Switzerland

2D laminae of transition metal dichalconide (TMDC) can construct a lamellar membrane to substitute the graphene oxide (GO) membranes for many reasons. To embody this stacking structure in a membrane format, we exfoliated MoS_2 powders chemically and prepared MoS_2-based lamellar membranes via vacuum filtration. Unlike the GO counterpart, MoS_2 lamellar membranes show excellent stability in a harsh aqueous environment (pH: 0.6-13.2), eliminating an unnecessary lamina-binding process and permitting regular interlamellar distance. Surface energy and XRD characterization confirm that the lamellar MoS_2 membrane maintains the similar structural configuration as the pristine one for very long soaked in a wide pH range of aqueous solutions. Not only sharing the similarity to GO such as gas tightness and unimpeded water vapour transmission, but the lamellar MoS_2 membrane also reveals molecular sieving towards organic vapours for the first time. With an average channel height of ~6.3 Å, the larger vapour molecules do not easily permeate through. Thanks to the high stability, this property enables the first observation of selective diffusion of ions through the 2D MoS_2 channels, attributable at a molecular level to a dehydration energy penalty, compatibility in the 2D aqueous hydrogen-bond network, and electrostatic interaction. Furthermore, we also demonstrate a promising catalyst material for a hydrogen evolution reaction (HER). By appropriate modification and configuration, more active sites and enhanced electron transfer have endowed such a lamellar MoS_2 membrane a promising catalytic performance towards hydrogen generation. With the high stability, the sieving performance and the HER activity, the MoS_2 lamella poses great potential in aqueous applications.

Keywords: MoS2 lamellar membrane, chemical stability, selective molecular transport, hydrogen evolution reaction

[O8.09]

Nanoporous graphene membranes for organic solvent nanofiltration

S. Zhang*[1,2], P. Kidambi[1], L. Wang[1], D. Jang[1], R. Karnik[1]

[1]Massachusetts Institute of Technology, USA, [2]National University of Singapore, Singapore

A large quantity of organic solvents are involved in fine chemical and pharmaceutical production, which leads to tremendous energy consumption due to the use of solvent evaporation for separation and serious environmental concerns. Nanofiltration membrane processes have been proposed in recent years as a more energy efficient way to separate the solvents. However, versatile membranes that are compatible with a range of solvents and also have the required selectivity are not readily available. With its atomic thickness, high mechanical and chemical stability, and the ability to sustain selective, sub-nanometer pores in its rigid lattice, nanoporous graphene has tremendous potential as a material for solvent filtration. Here we synthesized macroscopic, centimetre-scale atomically thin membranes from single layer graphene supported on porous supports into which selective sub-nanometer pores are introduced *via* nucleation and growth of pore defects. The membranes are used for the study of diffusive and pressure-driven transport of organic solvents across nanoporous graphene, as well as the demonstration of separation of model pharmaceutical molecules from organic solvent.

Keywords: Graphene, Organic solvent, Nanofiltration, thin membrane